published in
Croatica Chemica Acta 53 (1) 1 – 7 (1980)

	Serial	LITERATURE TYPE	A20	1 – 7	PAGES	
	Analytic	BIBLIOGR. LEVEL	A21	Nov. 5, 1979	RECEIPT	DATE
	541.18	UDC	A22	May 1980	PUBLICAT.	
A01	YU 0011–1643	ISSN	A23	English	TEXT	LANG
A02	CCACAA	CODEN	A24	Croat. Engl	SUMMARY	
A03	*Croat. Chem. Acta*	SHORT TITLE	A45	13	REFERENCES	
				2	TABLES	
A05	53 (1980)	VOL. NO. (YEAR)		4	FIGURES	
A06	No. 1	ISSUE NO.	CAT. OF CONTRIBUTION	Orig. Sci. Paper		
A07	*CCA – 1183*	OTHER IDENTIFIC.				

A08

STEADY - STATE RELAXATION TIMES FOR SURFACTANT FILMS AT THE WATER / AIR INTERFACE

A11

Đ. Dragčević and V. Pravdić

A14

Laboratory of Electrochemistry and Surface Phenomena, Center for Marine Research, 'Ruđer Bošković' Institute, P.O. Box 1016, 41001 Zagreb, Croatia, Yugoslavia

Dynamic surface tension *(1)* was used to study the relaxation times for two types of surfactant films, soluble sodium dodecylsulfate, and insoluble oleic acid, at the water/air interface. Surface tension was measured with a platinum Wilhelmy plate attached to an electrobalance in a PTFE lined Langmuir trough in which the surface was swept by PTFE sweepers at predetermined rates *(2)*. The output from the electrobalance and of the sweep mechanism was graphically recorded. The results of these recordings are shown in Fig. 1.

Relaxation times were determined in the steady state from the phase angle between the perturbation function (surface sweeping) and the response function (surface tension), in analogy with electrical phase angle phenomena by:

$$\tau = \frac{1}{e}\left(\frac{\tan \Delta\phi}{2\pi f}\right)$$

where τ is the relaxation time, $\Delta\phi$ the phase angle and $\omega = 2\pi f$ is the angular excitation frequency (sweep rate).

DESCRIPTORS

Relaxation
  of surfactant films at water/air interface,

Surface tension
  dynamic
    measurement techniques for,
    relaxation times for,

Surfactants
  films on water, measurement of relaxation times,

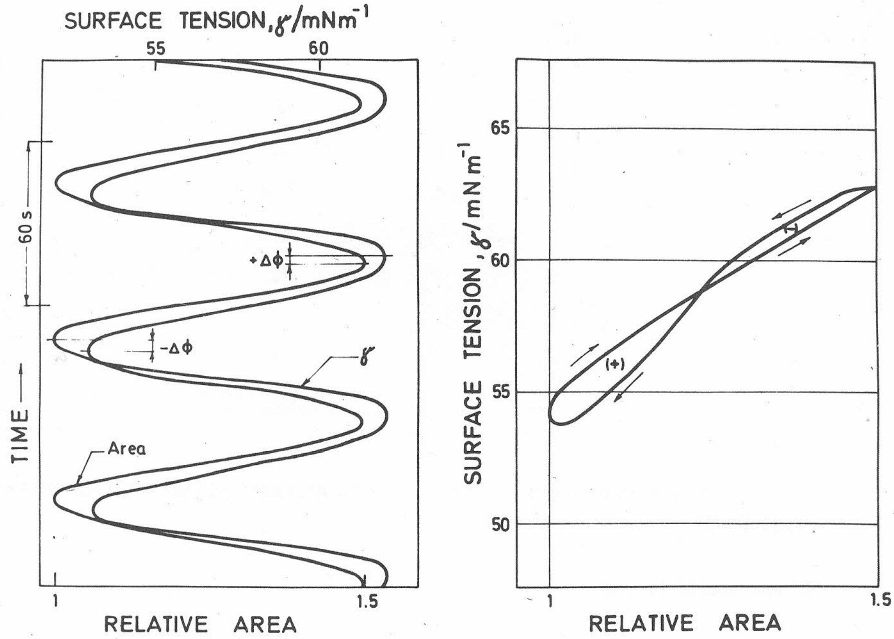


Fig. 1

Dynamic surface tension of oleic acid recorded on two recorders. The left hand side shows 2 sinusoidal functions, surface area ('area') and surface tension (γ), with the resulting phase shift $\Delta\phi$, recorded on a x_1, x_2 - time recorder. The right hand side shows the surface tension - area hysteresis curve for the same experiment, recorded on a x - y recorder.

The calculated values for the relaxation times of oleic acid films on water were between 0.25 and 1.25 s, and were inversely proportional to both the rate of sweeping and to the concentration of molecules in the surface film. For the soluble surfactant, sodium dodecylsulfate, the relaxation times were reaching a minimum value of 0.2 s, at a bulk concentration between 9.1 and 18.3 μmol dm^{-3}

REFERENCES

1. R. Bienkowski and M. Skolnick *J.Colloid Interface Sci.* 39 (1972) 323.
2. R. M. Mendenhall and A. L. Mendenhall, Jr., *Rev.Sci.Instr.* 34 (1963) 1350.

Abstractor: Đ. Dragčević

published in
Croatica Chemica Acta 53 (1) 9 – 23 (1980)

	Serial	LITERATURE TYPE	A20	9 – 23	PAGES
	Analytic	BIBLIOGR. LEVEL	A21	May 5, 1979	RECEIPT DATE
	541.183	UDC	A22	May 1980	PUBLICAT.
A01	YU 0011–1643	ISSN	A23	English	TEXT LANG
A02	CCACAA	CODEN	A24	Croat. Engl.	SUMMARY
A03	*Croat. Chem. Acta*	SHORT TITLE	A45	22	REFERENCES
				1	TABLES
A05	53 (1980)	VOL. NO. (YEAR)		3	FIGURES
A06	No. 1	ISSUE NO.	CAT. OF CONTRIBUTION		Conference Paper
A07	*CCA – 1184*	OTHER IDENTIFIC.			

A08

STUDIES OF ADSORPTION FROM GASEOUS AND LIQUID MIXTURES ON SOLIDS OF *QUASI*- GAUSSIAN ENERGY DISTRIBUTION

A11

A. Patrykiejew, M. Jaroniec, A. Dabrowski, and J. Tóth

A14

Department of Theoretical Chemistry, Institute of Chemistry, MCS University, Lublin, Poland, and Petroleum Engineering Research Laboratory of the Hungarian Academy of Sciences, Miskolc, Hungary

DESCRIPTORS

Adsorption
of gas-liquid mixtures, theory of,
on heterogeneous solid surfaces,

Mixtures
gas-liquid, adsorption on heterogeneous solid surfaces of,

Surface
heterogeneous solid, adsorption of gas-liquid mixtures on,

One of the empirical equations describing the adsorption on heterogeneous surfaces have been proposed by Tóth in an earlier paper *(1)*:

$$N(p) = N_c\left[p^m/(b \quad + p^m)\right]^{1/m} \qquad (1)$$

where N is the adsorbed amount, N_c is a constant connected with molecular capacity, m is heterogeneity parameter from the interval (0,1), and b^* is a constant connected with the characteristic adsorption energy.

In this paper a modification of eqn. (1) is proposed so that $b^* = b^m$, where

$$b = K\exp(-\epsilon_0/kT).$$

ϵ_0 is the adsorption energy of a homogeneous surface, K is a constant connected with the molecular partition functions in the adsorbed and in the gas phase, and kT have their usual meanings. Experiments with hydrocarbons adsorption on charcoal 'Nuxit-Al' proved *(2)* that m parameter is a function of temperature. By differentiation of the logarithm of both sides of modified eqn.(1) with respect to temperature, introducing $\Theta = N(p)/N(p_o)$, leads to the expression for overall isosteric heat of adsorbtion $\hat{Q}^{st}$. Assuming that *m* is a linear function of T then $\hat{Q}^{st}$ becomes:

$$\hat{Q}^{st} = RT^2 \, (d \ln b/dT) + RT^2 \eta \, . \, F(\Theta) \qquad (2)$$

where

$$F(\Theta) = \frac{1}{m} \ln (1.\Theta^m) \, . \, \frac{\Theta^m \ln \Theta}{m(1-\Theta m)}$$

Function $F(\Theta)$ is presented in Fig. 1. for different values of *m* parameter.

On the basis of the above discussion the eqn. of van Dongen and Broekhoff *(3)* is generalised, so as to take into account the temperature dependence of the energy distribution function:

$$\hat{Q}^{st} = Q^{st} - \Delta \hat{Q}^{st} \qquad (3)$$

where Q^{st} is the isosteric heat of adsorption derived by previous authors *(3)* and $\Delta\hat{Q}^{st}$ is a correction term associated with making allowances for temperature dependence of the energy distribution function. The modified adsorption isotherm is also generalised for the case of adsorption from multicomponent gas and liquid mixtures on solids of *quasi*-gaussian energy distribution.

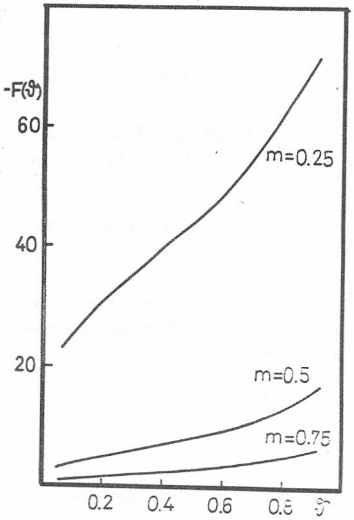


Fig. 1

REFERENCES

1. J. Tóth, *Acta Chem.Acad.Sci.Hung.* 69 (1971) 311.
2. M. Jaroniec and J. Tóth, *Colloid Polymer Sci.* 254 (1976) 641.
3. R. H. van Dongen and J. C. P. Broekhoff, *Surface Sci.* 18 (1969) 462.

Abstractor: I. Ružić

published in
Croatica Chemica Acta 53 (1) 25 – 32 (1980)

	Serial	LITERATURE TYPE	A20	25 – 32	PAGES	
	Analytic	BIBLIOGR. LEVEL	A21	May 24, 1979	RECEIPT	DATE
	541.128	UDC	A22	May 1980	PUBLICAT.	
A01	YU 0011–1643	ISSN	A23	English	TEXT	LANG
A02	CCACAA	CODEN	A24	Croat. Engl.	SUMMARY	
A03	*Croat. Chem. Acta*	SHORT TITLE	A45	11	REFERENCES	
				1	TABLES	
A05	53 (1980)	VOL. NO. (YEAR)		2	FIGURES	
A06	No. 1	ISSUE NO.	CAT. OF CONTRIBUTION	Orig. Sci. Paper		
A07	*CCA – 1185*	OTHER IDENTIFIC.				

A08

ESTERIFICATION OF *n*-BUTANOL WITH ACETIC ACID CATALYZED BY A CATION EXCHANGE RESIN. EFFECT OF CATALYTIC ACTIVITY ON REACTION KINETICS

A11

Z. Gomzi and S. Zrnčević

A14

Faculty of Technology, University of Zagreb, 41000 Zagreb, Croatia, Yugoslavia

DESCRIPTORS

Esterification catalysts
ion-exchangers, for acetic acid by *n*-butanol,

Ion-exchangers
as catalysts for esterification,

Kinetics of esterification
of acetic acid by *n*-butanol, catalyst effect on,

Kinetics of the esterification of *n*-butanol with acetic acid was investigated in batch and tubular reactors using a cation exchanger - a microporous polystyrene resin - as a catalyst. Batch experiments were performed at 85 °C using either a completely dried ion exchanger or one whose water content had been adjusted to 27%. The extent of reaction was followed by titrating acetic acid at suitable time intervals. In the experiments with tubular reactor the experiments were started with dry ion exchanger (at 55 °C); in these experiments the height of the resin bed was also measured, in addition to the amount of acetic acid.

Several possible mechanistic models were checked by a least-squares numerical analysis. It was found that the best fit to the experimental data in batch experiments with partly wet resin is achieved by assuming a pseudohomogeneous kinetics *(1)* while for the experiments with dry resin a model derived from heterogeneous kinetics in which the surface reaction of chemisorbed acid and adsorbed alcohol is believed to be the rate-determining step.

The investigations of the induction period in the experiments with tubular reactor showed a marked influence of the water content on the catalytic activity of the resin during the reaction. From Fig. 1 it is seen that the reactor reaches the steady state

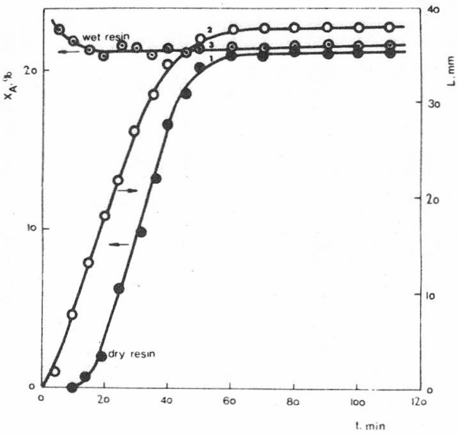


Fig. 1

sooner if it is filled with already wet resin (curve 2) than in the case of dry catalyst (curve 1). Steady state conversion is nevertheless the same; a stationary conversion can be obtained only when the resin height becomes constant (*cf.* curves 1 and 3). It was shown that the change of the catalyst activity during the induction period can be ascribed to the diffusion of the reactants into resin particles.

REFERENCE

1. C. K. Ingold, *Structure and Mechanism in Organic Chemistry,* Cornell Univ. Press, Ithaca N.Y. 1968.

Abstractor: Vl. Simeon

published in
Croatica Chemica Acta 53 (1) 33 – 43 (1980)

	Serial	LITERATURE TYPE	A20	33 – 43	PAGES	
	Analytic	BIBLIOGR. LEVEL	A21	July 25, 1979	RECEIPT	DATE
	547.77	UDC	A22	May 1980	PUBLICAT.	
A01	YU 0011–1643	ISSN	A23	English	TEXT	LANG
A02	CCACAA	CODEN	A24	Croat. Engl.	SUMMARY	
A03	*Croat.Chem.Acta*	SHORT TITLE	A45	12	REFERENCES	
				1	TABLES	
A05	53 (1980)	VOL. NO. (YEAR)		1	FIGURES	
A06	No. 1	ISSUE NO.	CAT. OF CONTRIBUTION	Orig. Sci. Paper		
A07	*CCA – 1186*	OTHER IDENTIFIC.				

A08

MASS SPECTRAL FRAGMENTATION STUDY OF SUBSTITUTED 1,3-DIPHENYL-2-PYRAZOLINES

A11

D. Srzić, L. Klasinc, W. Seitz, and H. Guesten

A14

'Ruđer Bošković' Institute, P.O. Box 1016, 41001 Zagreb, Croatia, Yugoslavia, and Kernforschungszentrum Karlsruhe, Institut fuer Radiochemie, Karlsruhe, Federal Republic of Germany

Twenty two 1,3-diphenyl-2-pyrazolines monosubstituted in one or both phenyls with SO_2Me, SO_2NH_2 SMe, NHCOMe, $CONH_2$, COOMe, $N(Me)_2$, and Cl, as well as disubstituted and trisubstituted in one or both phenyls with Me and OMe, were studied.

In discussing the behaviour of substituted 1,3-diphenyl-2-pyrazolines with respect to the electron impact, the attention was especially paid to the effect of the

i) monosubstitution of one or both phenyls
ii) polysubstitution of one or both phenyls

According to their characteristics the mass spectra of 1,3-diphenyl-2-pyrazolines monosubstituted in one or both phenyls can be divided into three groups *(1)*:

1) 1,3-diphenyl-2-pyrazolines, having the substituent relatively tightly bonded, fragment from the molecular ion in the same manner as the unsubstituted compound *(2)* [here $N(Me)_2$].

2) 1,3-diphenyl-2-pyrazolines of this group readily lose their substituents or parts of substituents and are fragmentized further from the (M-substituent)+ ion in the same way as the parent compound (here SO_2Me, SMe, NHCOMe, and $CONH_2$).

3) 1,3-diphenyl-2-pyrazolines which show new types of fragmentation and involve the substituent in the possible rearrangement reactions prior to fragmentation (no example in this study).

DESCRIPTORS

Mass spectroscopy
fragmentation patterns for substituted pyrazolines,

Pyrazoline, derivatives
substituted 1,3-diphenyl, mass spectral fragmentation of,

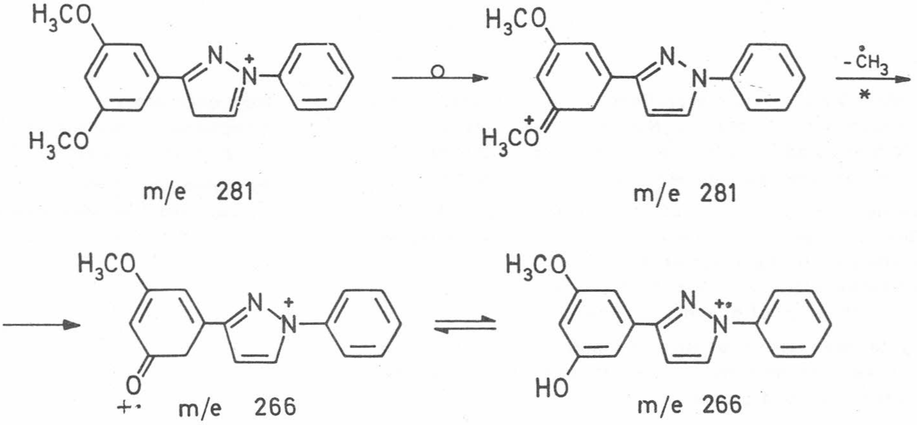
The fragmentation of the 1,3-diphenyl-2-pyrazolines monosubstituted in both phenyls can easily be rationalized on the basis of the behaviour of corresponding compounds monosubstituted in one phenyl. Furthermore, the comparison of mass spectra of two compounds monosubstituted in one phenyl with the corresponding compound monosubstituted in both phenyls indicates that neither the stability of the molecular ion nor the intensities of analoguous ions are changed significantly, which implies the nonexistence (or unimportance) of synergistic substituent effects.

The polymethoxy substituted 1,3-diphenyl-2-pyrazolines, similarly to the monomethoxy compounds, undergo two characteristic primary fragmentation reactions, namely, loss of H and Me. A very important secondary fragmentation process is elimination of CO from the $(M-Me)^+$ ions.

The abundance of the $(M-H)^+$ ion in the mass spectra of dimethoxy and trimethoxy substituted compounds varies from 1 to 39% of the molecular ion. In this study, using the hexadeuterodimethoxy compound, ring and methoxy hydrogens were distinguished. Loss of a methoxy hydrogen was negligible.

If the methoxy groups are *ortho* or *para* each to other, more favourable fargmentations like methyl loss prevail over the hydrogen loss due to the stable quinoid structure of the resulting $(M-Me)^+$ ion. The low intensity of the $(M-Me)^+$ ion in the mass spectra of the compound with two *meta* methoxy groups is ascribed to its unability to form a quinoid structure. However, the loss of methyl from the $(M-H)^+$ ion in this compound indicates possible rearrangements within the molecular ion stabilizing the resulting $(M-Me)^+$ ion (Scheme 1).

Scheme 1



REFERENCES

1. D. Srzić, Z. Orhanović, L. Klasinc, and H. Guesten, *Advan. Mass Spectrom.* 8 (1980) in press.

2. D. Srzić, L. Klasinc, H. E. Noppel, and H. Guesten, *Org. Mass Spectrom.* 13 (1980) 30.

Abstractor: D. Srzić

published in
Croatica Chemica Acta 53 (1) 45 – 50 (1980)

	Serial	LITERATURE TYPE	A20	45 – 50	PAGES	
	Analytic	BIBLIOGR. LEVEL	A21	July 25, 1979	RECEIPT	DATE
	539.19	UDC	A22	May 1980	PUBLICAT.	
A01	YU 0011–1643	ISSN	A23	English	TEXT	LANG.
A02	CCACAA	CODEN	A24	Croat. Engl.	SUMMARY	
A03	*Croat. Chem. Acta*	SHORT TITLE	A45	12	REFERENCES	
				–	TABLES	
A05	53 (1980)	VOL. NO. (YEAR)		–	FIGURES	
A06	No. 1	ISSUE NO.	CAT. OF CONTRIBUTION	Orig. Sci. Paper		
A07	*CCA – 1187*	OTHER IDENTIFIC.				

A08

ESTIMATION OF THE HOMO-LUMO SEPARATION

A11 *A. Graovac and I. Gutman*

A14 'Ruđer Bošković' Institute, P.O. Box 1016, 41001 Zagreb, Croatia, and Faculty of Science, P.O. Box 60, 34001 Kragujevac, Serbia, Yugoslavia

In the quantum theory of the electronic structure of molecules, the difference between the energy of the highest occupied molecular orbital (HOMO) and the energy of the lowest unoccupied molecular orbital (LUMO), the so called HOMO-LUMO separation, *S*, plays an important role. In spite of several attempts in the past *(1,2)*, the structural factors which influence *S* are not yet clear.

In the present work a number of new results on *S* is reported. The first and the second order approximate topological formula for *S* of alternant conjugated hydrocarbons are given. The accuracy of the approximate formulae was tested on 70 alternant systems. Although the dependence of *S* on topology is rather complex indeed, gross part of *S* is reproduced by a relatively simple topological function *H*. The explicit relation between *H* and the topology of the corresponding molecule is known *(3,4)*.

Non-alternant hydrocarbons and heteroconjugated systems are treated in the Appendix.

DESCRIPTORS

Hydrocarbons, properties
conjugated, HOMO-LUMO separation for,

Mathematics
graph theory, for estimation of HOMO-LUMO separation for conjugated hydrocarbons,

Molecular orbital
HOMO-LUMO
topological formulae for,
of alternant conjugated hydrocarbons,

1. G. G. Hall, *Mol.Phys.* 33 (1977) 551.
2. I. Gutman, and D. H. Rouvray, *Chem.Phys.Lett.* 62 (1979) 384.
3. C. F. Wilcox, *J.Amer.Chem.Soc.* 91 (1969) 2732.
4. C. F. Wilcox, I. Gutman, and N. Trinajstić, *Tetrahedron* 31 (1975) 147.

Abstractor: A. Graovac

published in

Croatica Chemica Acta 53 (1) 51 – 68 (1980)

	Serial	LITERATURE TYPE	A20	51 – 68	PAGES	
	Analytic	BIBLIOGR. LEVEL	A21	October 1, 1979	RECEIPT	DATE
	539.19	UDC	A22	May 1980	PUBLICAT.	
A01	YU 0011–1643	ISSN	A23	English	TEXT	LANG
A02	CCACAA	CODEN	A24	Croat. Engl.	SUMMARY	
A03	*Croat. Chem. Acta*	SHORT TITLE	A45	37	REFERENCES	
				–	TABLES	
A05	53 (1980)	VOL. NO. (YEAR)		17	FIGURES	
A06	No. 1	ISSUE NO.	CAT. OF CONTRIBUTION	Orig. Sci. Paper		
A07	*CCA – 1188*	OTHER IDENTIFIC.				

A08

POTENTIAL SURFACE STUDIES OF OPEN SHELL SYSTEMS

A11 *P. Bischof*

A14 Institut für Organische Chemie der THD, D 6100 Darmstadt, Germany

The electronic structure of a large number of organic radicals was examined by using the developed unrestricted version of the semiempirical MINDO/3 method *(1,2)*. A review of the obtained results *(2-4)* is presented. The calculated heats of formation (ΔH_f) are generally in good agreement with available experimental data. The estimated ΔH_f values are usually too low ~ 40 kJ/mole. This is not a serious drawback and had to be expected from the single determinant approach. However, it only shifts the origin of the energy scale. The relative stabilities of radical isomers are in most cases predicted quite correctly. Theoretical interatomic distances are in reasonably good accordance with experiment.

Particular emphasis is placed on the discussion of the reactivity of radicals and reaction paths. Theoretical results are here of utmost importance because the elementary reaction steps in radical rearrangements are extremely difficult to access by conventional experimental techniques. An original procedure for searching and verifying local minima and saddle points on the energy hypersurfaces is discussed. This approach is applied on the series of ω-alkenyl radicals and their routes of cyclisations were throughly investigated. The experimental findings can be rationalised by a simple orbital overlap model which on the other hand leads to a natural link to the allowed/forbidden

DESCRIPTORS

Heat of formation
of open shell systems, MINDO/3 calculation for,

Molecular orbital
MINDO/3 calculation of open shell systems,

Potential energy and function
surface of open shell systems, MO calculation of,

concept. These findings are corroborated by the available pieces of experimental evidence. An important outcome of the analysis is that, unlike for closed shell systems, the activated complexes of forbidden reactions for doublet states (Fig. 1) can be successfully described by single configuration and should therefore be accessible by appropriate semiempirical treatments.

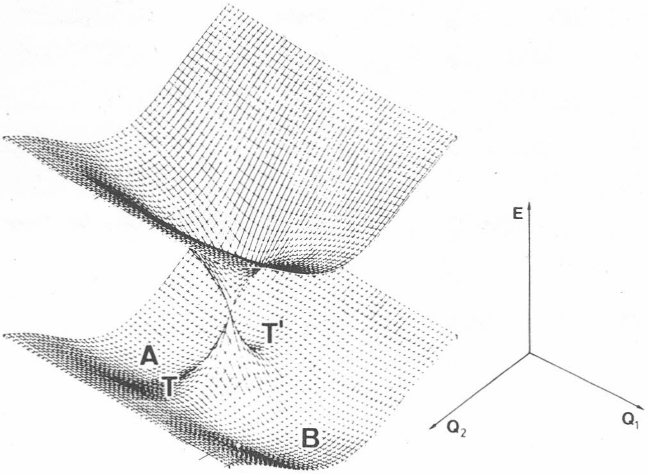


Fig. 1

Model potential surface of a 'forbidden' doublet reaction.

REFERENCES

1. R. C. Bingham, M. J. S. Dewar, and D. H. Lo. *J.Amer.Chem.Soc.* 97 (1975) 1285.
2. P. Bischof, *J.Amer.Chem.Soc.* 98 (1976) 6844.
3. P. Bischof, *Tetrahedron Lett.* 15 (1979) 1291.
4. P. Bischof, *J.Amer.Chem.Soc.* 99 (1977) 8145.

Abstractor: L. Klasinc

published in

Croatica Chemica Acta 53 (1) 69 – 79 (1980)

	Serial	LITERATURE TYPE	A20	69 – 79	PAGES
	Analytic	BIBLIOGR. LEVEL	A21	Sept. 7, 1979	RECEIPT (DATE)
	547.8	UDC	A22	May 1980	PUBLICAT. (DATE)
A01	YU 0011–1643	ISSN	A23	English	TEXT (LANG)
A02	CCACAA	CODEN	A24	Croat. Engl.	SUMMARY (LANG)
A03	*Croat.Chem.Acta*	SHORT TITLE	A45	14	REFERENCES
				7	TABLES
A05	53 (1980)	VOL. NO. (YEAR)		–	FIGURES
A06	No. 1	ISSUE NO.	CAT. OF CONTRIBUTION	Orig. Sci. Paper	
A07	*CCA – 1189*	OTHER IDENTIFIC.			

A08

THIOAMIDES. XV. SOME NEW SUBSTITUTED 2-(2- OR 3-FURYL)-BENZOTHIAZOLES. THE PREPARATION AND PROPERTIES

A11

L. Fišer-Jakić, B. Karaman, and K. Jakopčić

A14

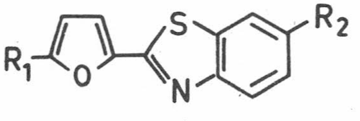
Laboratory of Organic Chemistry, Faculty of Technology, University of Zagreb, 41000 Zagreb, Croatia, Yugoslavia

DESCRIPTORS

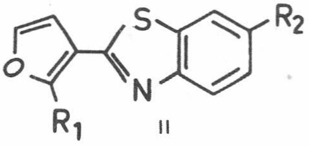
Benzothiazole,
—, 2-furyl
preparation of,
quarternization by dimethylsulfate,
—, 3-furyl
preparation of,

Benzothiazoles are the class of heterocyclic compounds possessing a weak basic character *(1,2)* which is influenced by substituents according to their electronic effect. On alkylation they can give quarternary salts *(3,4)*. Suprisingly, only a few examples of 2-furyl and none of 3-furyl substituted benzothiazole salts are known.

In this work the preparation of several 2-furyl- and 2-(3-furyl)-benzothiazoles (I and II) are described, through cyclisation of corresponding *N*-aryl-thiofuranamides with ferricyanides *(5)*.

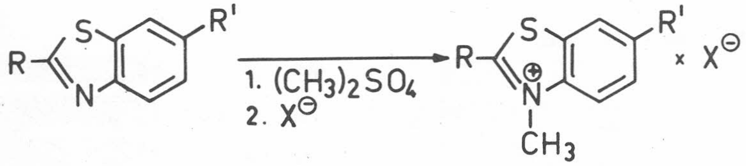


I



II

Some of the prepared benzothiazoles *i.e.* 2-(2-methyl-3-furyl)- and 6-methyl-2-(2-methyl-4-furyl)- benzothiazole gave stable hydrochlorides. The isomeric 5-methyl-2-furylbenzothiazole fail to form hydrochloride, what lead to a conclusion, that positive electronic effect of methyl group close to the thiazole ring, increases electron density on the nitrogen. The effects of substituent on benzothiazole basicity were recognized in different rates of quarternization with dimethylsulphate (Scheme 1).



Scheme 1

REFERENCES

1. R. M. Acheson, *An Introduction to the Chemistry of Heterocyclic Compounds,* Interscience Publ. Inc. New York 1960, p. 278.
2. A. Albert, R. Goldacre, and J. Phillips, *J.Chem.Soc.* (1948) 2240.
3. A. I. Kiprianov and A. A. Schulezhko, *Zh.Obsch.Khim.* 34 (1964) 3932.
4. H. Quast and E. Schmidt, *Chem.Ber.* 101 (1968) 4012.
5. P. Jacobson, *Chem.Ber.* 19 (1886) 1067.

Abstractor: M. V. Proštenik

published in
Croatica Chemica Acta 53 (1) 81 – 85 (1980)

	Serial	LITERATURE TYPE	A20	81 – 85	PAGES	
	Analytic	BIBLIOGR. LEVEL	A21	Jan. 5, 1979	RECEIPT	DATE
	546.883	UDC	A22	May 1980	PUBLICAT.	
A01	YU 0011–1643	ISSN	A23	English	TEXT	LANG
A02	CCACAA	CODEN	A24	Croat. Engl.	SUMMARY	
A03	*Croat. Chem. Acta*	SHORT TITLE	A45	6	REFERENCES	
				–	TABLES	
A05	53 (1980)	VOL. NO. (YEAR)		–	FIGURES	
A06	No. 1	ISSUE NO.	CAT. OF CONTRIBUTION	Orig. Sci. Paper		
A07	*CCA – 1190*	OTHER IDENTIFIC.				

A08

SPECTROPHOTOMETRIC DETERMINATION OF TANTALUM(V) WITH 5–IODO–8–HYDROXYQUINOLINE–7–SULPHONIC ACID

A11

Y. Sharma

A14

Department of Chemistry, Ganjdundwara College, Ganjdundwara, Etah, U.P., India

A spectrophotometric method for the determination of microgram amounts of tantalum(V) utilizing the 5-iodo-8-hydroxyquinoline-7-sulphonic acid has been investigated. Tantalum(V) reacts with the quoted reagent to form a yellowish coloured complex having maximum absorbance at 405 nm in citric acid medium at pH 6.3, with a molar absorptivity of $5.753 \cdot 10^4$ mol^{-1} dm^2. Beer's law is valid over the concentration range of 1–7.5 µg tantalum(V) ml^{-1}. The mole ratio method was applied to determine the composition of the complex. The observations confirm the 1:2 ratio of metal to ligand. The overall stability constant was determined from mole ratio plots and was found for log $K = 8.53$.

The following ions with their amounts in ppm given in parenthesis did not cause more than a ± 3% change in absorbance: $C_2O_4^{2-}$ (400), NO_3^- (450), Cl^- (60), Br^- (50), F^- (40), Al^{3+} (150), Zn^{2+} (180) Mn^{2+} (200), Cu^{2+} (150), Co^{2+} (140) Ba^{2+} (220), Ca^{2+} (200), Ni^{2+} (160), Pb^{2+} (50), PO_4^{3-} (50), Cr^{3+} (120), BO_3^{3-} (30), Fe^{3+} (40), V(V) (350), Nb(V) (250), Mo(VI) (250), W(VI) (50).

DESCRIPTORS

Quinoline-8-hydroxy,
—, 5-iodo-7-sulfonic acid
reagent for tantalum(V),

Spectrochemical analysis
spectrophotometric, determination of tantalum(V),

Tantalum(V)
spectrophotometric determination of,

REFERENCES

1. J. Cooper, *J.Amer.Chem.Soc.* 63 (1941) 437.
2. E. Kirby and H. Freiser, *J.Phys.Chem.* 65 (1961) 191.
3. R. Puschel and E. Lassner, *Z.Anorg,Algem.Chem.* 326 (1964) 317.
4. S. V. Elinson, *Zh.Anal.Khim.* 20 (1965) 676.

Abstractor: I. Piljac

published in
Croatica Chemica Acta 53 (1) 87 – 91 (1980)

	Serial	LITERATURE TYPE	A20	87 – 91	PAGES	
	Analytic	BIBLIOGR. LEVEL	A21	May 14, 1979	RECEIPT	DATE
	546.72	UDC	A22	May 1980	PUBLICAT.	
A01	YU 0011–1643	ISSN	A23	English	TEXT	LANG
A02	CCACAA	CODEN	A24	Croat. Engl.	SUMMARY	
A03	*Croat. Chem. Acta*	SHORT TITLE	A45	15	REFERENCES	
				1	TABLES	
A05	53 (1980)	VOL. NO. (YEAR)		1	FIGURES	
A06	No. 1	ISSUE NO.	CAT. OF CONTRIBUTION	Note		
A07	*CCA – 1191*	OTHER IDENTIFIC.				

A08

EXTRACTIVE SPECTROPHOTOMETRIC DETERMINATION OF IRON(III) WITH *N*-HYDROXY-*N*-*p*- CHLOROPHENYL–*N'*-(2-METHYL)-PHENYL-*p*-TOLUAMIDINE HYDROCHLORIDE IN THE PRESENCE OF THIOCYANATE

A11

P. K. Sharma and R. K. Mishra

A14

Department of Chemistry, Ravishankar University, Raipur, 492010 M.P., India

A new reagent, *N*-hydroxy-*N*-*p*-chlorophenyl-*N'*-2-methyl-phenyl-*p*-toluamidine hydrochloride (HCMPMPTH) is proposed for the extraction and quantitative spectrophotometric determination of microgram amounts of Fe(III) in the presence of thiocyanate. The orange species was determined to be 1:1:2 (Fe:HCPMPTH:thiocyanate) ternary complex with a sharp absorption maximum at 460 nm and a molar absorption coefficient of 12565 dm^3 mol^{-1} cm^{-1} (in benzene).

Conditions for the analytical application : acidity (hydrochloric acid) (0.10...1.20) mol dm^{-3}, reagent excess 30 fold (HCPMPTH) and 240 fold (thiocyanate), extraction in 2 min, temperature (20...40°C), foreign components (Cl$^-$, Br$^-$, NO$_3^-$ SO$_4^{2-}$, NH$_3$, phthalate, borate, alkaline earths and lanthanides) do not interfere in 500 fold excess to Fe. Optimum Fe concentration: (o.8...4.0) ppm. The method is applicable for selective extraction in the presence of Fe^{2+}, Mo^{6+}, W^{6+}, Ni^{2+}, Al^{3+}, Zn^{2+} and Cr^{3+}.

DESCRIPTORS

Spectrochemical analysis
extractive spectrophotometric,
determination of iron(III),

Iron(III)
extractive spectrophotometric
determination of,

Abstractor: Z. Meić

published in
Croatica Chemica Acta 53 (1) 93 – 99 (1980)

	Serial	LITERATURE TYPE	A20	93 – 99	PAGES	
	Analytic	BIBLIOGR. LEVEL	A21	March 27, 1979	RECEIPT	DATE
	546.49	UDC	A22	May 1980	PUBLICAT.	
A01	YU 0011–1643	ISSN	A23	English	TEXT	LANG
A02	CCACAA	CODEN	A24	Croat. Engl.	SUMMARY	
A03	*Croat.Chem.Acta*	SHORT TITLE	A45	22	REFERENCES	
				–	TABLES	
A05	53 (1980)	VOL. NO. (YEAR)		3	FIGURES	
A06	No. 1	ISSUE NO.	CAT. OF CONTRIBUTION	Orig. Sci. Paper		
A07	*CCA – 1192*	OTHER IDENTIFIC.				

A08

MODEL STUDIES OF THE SOLUBILITY OF INORGANIC MERCURY IN THE POLLUTED COASTAL MARINE ENVIRONMENT

A11

*H. Bilinski and S. Jusufi**

A14

Department of Physical Chemistry, 'Ruđer Bošković' Institute, P.O. Box 1016, 41001 Zagreb, Croatia, and
*Department of Chemistry, University of Priština, 38000 Priština, Kosovo, Yugoslavia

The solubility of inorganic mercury in polluted sea water was investigated by determining Hg by atomic absorption spectrophotometry in solutions with varying amount of sea water, $[CO_3^{-2}]$ and pH. The solubility of HgS(s) increases with increasing pH and $[CO_3^{-2}]$. At $[NaHCO_3] = 10^{-3}$ mol dm^{-3}, concentration which is characteristic for sea water, the mercury concentration (*ca.* 40 μg dm^{-3}) does not change upon the dillution.

Model equilibrium calculations showed that, in the presence of oxygen, mercury containing sediments can release some mercury, presumably as $Hg^0(aq)$ which stands in equilibrium with $Hg^0(g)$. The rate of mercury dissolution was not estimated but some findings *(1,2)* give support to the above theoretical conclusion. Therefore, one could predict a continuous leaching of soluble mercury from polluted sediments a long time after their deposition.

DESCRIPTORS

Environment
  marine coastal polluted
    model studies for,
    solubility of inorganic mercury
      in,

Mercury(II)
  in seawater
    determination of,
    leaching from polluted sediments,
    solubility of,

Water pollution
  by mercury compounds,

REFERENCES

1. L. Kosta, V. Ravnik, A.R. Byrne, J. Stirn, M. Dermelj, and P. Stegnar, *J.Radioanal.Chem.* 44 (1978) 317.
2. R. R. Turner and S.E. Lindberg, *Env.Sci.Technol.* 12 (1978) 918.

Abstractor: Vl. Simeon

published in

Croatica Chemica Acta 53 (1) 101 – 105 (1980)

	Serial	LITERATURE TYPE	A20	101 – 105	PAGES	
	Analytic	BIBLIOGR. LEVEL	A21	Jan. 28, 1980	RECEIPT	DATE
	541.135.52	UDC	A22	May 1980	PUBLICAT.	DATE
A01	YU 0011–1643	ISSN	A23	English	TEXT	LANG
A02	CCACAA	CODEN	A24	Croat. Engl.	SUMMARY	LANG
A03	*Croat. Chem. Acta*	SHORT TITLE	A45	12	REFERENCES	
				–	TABLES	
A05	53 (1980)	VOL. NO. (YEAR)		3	FIGURES	
A06	No. 1	ISSUE NO.	CAT. OF CONTRIBUTION	Prelim. Comm.		
A07	*CCA – 1193*	OTHER IDENTIFIC.				

A08

A DEVICE FOR VIBRATING DROPPING MERCURY ELECTRODE

A11 *T. Magjer, M. Lovrić, and M. Branica*

A14 Center for Marine Research, 'Ruđer Bošković' Institute, P.O.Box 1016, 41001 Zagreb, Croatia, Yugoslavia

The vibrating dropping mercury electrode (VDME) can be successfully applied in the cases when the measurements with the dropping mercury electrode (DME) are difficult to perform because of the inhibitions of the electrode reaction by the adsorption of some surface active substances.

The main disadvantage of the devices for the VDME described in the literature *(1,2)* are a very complex construction and a varying number of drops per seconds.

A newly developed device for the VDME is described (Fig. 1). The mechanism is simplified and the reproducibility of the dropping time is improved. The vibrating device consists of a synchronous electric motor and a set of axles, each of them with a different profile at the free end. Every time the sharp edge of the axle hits the capillary, over the plastic hammer, one drop is torn off.

The applicability of the new electrode for the measurements of polarographic waves in the presence of surface active blocking substances is reported. The possibilities of the VDME for the speciation of certain metal ions in multiligand systems are discussed.

DESCRIPTORS

Apparatus
construction of vibrating dropping mercury electrode,

Electrodes
vibrating dropping mercury
application of,
construction of a new device,

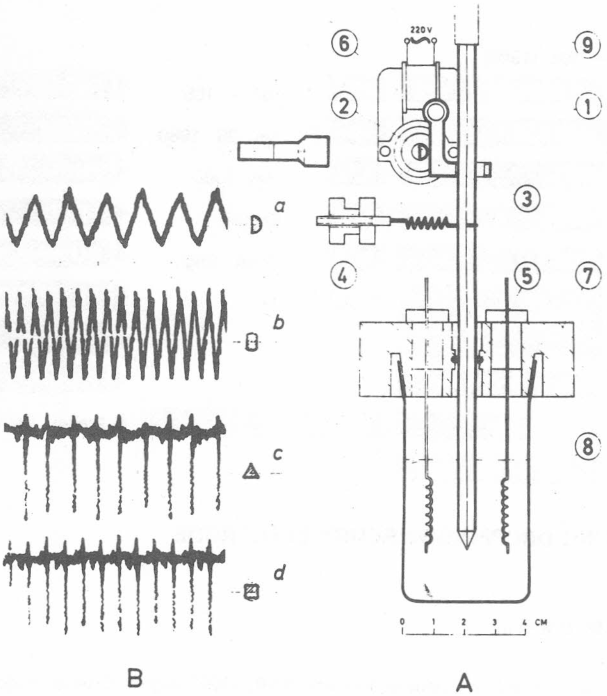


Fig. 1.

A) The scheme of the vibrating dropping mercury electrode, 1 - capillary; 2 - axle; 3 - plexy hammer; 4 - spring; 5 - rubber O-ring; 6 - electromotor; 7 - plexiglass cover of the cell; 8 - polyethylene cell (100 ml); 9 - tygon tube.

B) The oscillographic measurements of the reproducibility of the drop size and dropping rate a) 25 drops per second, b) 50 drops per second, c) 75 drops per second, d) 100 drops per second.

REFERENCES

1. D. A. Berman, P. R. Saunders, and R. J. Winzler, *Anal. Chem.* 23 (1951) 1040.
2. R. E. Cover and J. G. Connery, *Anal. Chem.* 41 (1969) 918.

Abstractor: M. Branica

published in
Croatica Chemica Acta 53 (1) 107 – 113 (1980)

	Serial	LITERATURE TYPE	A20	107 – 113	PAGES
	Analytic	BIBLIOGR. LEVEL	A21	Feb. 6, 1980	RECEIPT DATE
	577.17.37:54.057	UDC	A22	May 1980	PUBLICAT. DATE
A01	YU 0011–1643	ISSN	A23	English	TEXT LANG
A02	CCACAA	CODEN	A24	Croat. Engl.	SUMMARY LANG
A03	*Croat. Chem. Acta*	SHORT TITLE	A45	13	REFERENCES
				1	TABLES
A05	53 (1980)	VOL. NO. (YEAR)		4	FIGURES
A06	No. 1	ISSUE NO.	CAT. OF CONTRIBUTION	Orig. Sci. Paper	
A07	*CCA – 1194*	OTHER IDENTIFIC.			

A08

PREPARATION OF Des–ALANINE–B^{30}–INSULIN *via* TRYPTIC HYDROLYSIS OF PORCINE INSULIN MODIFIED AT THE ARGINYL RESIDUE BY CYCLOHEXANE–1,2–DIONE

A11

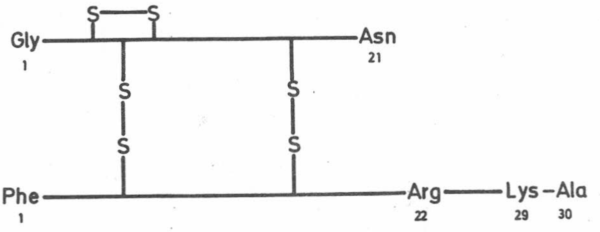
B. Mulac and D. Keglević

A14

Tracer Laboratory, Department of Organic Chemistry and Biochemistry, 'Ruđer Bošković' Institute, P.O.Box 1016, 41001 Zagreb, Croatia, Yugoslavia

Selective modification of the arginyl residue in insulin by the method of Patthy and Smith *(1)*, involving reversible reaction of cyclohexane-1,2-dione (CHD) in borate buffer with the guanidino function of arginine, was studied. It is shown that CHD reacts exclusively with the Arg-B^{22} residue in the insulin molecule to give the modified peptide in which the complexed Arg residue is resistant to the action of trypsin, thus enabling selective cleavage at the Lys-B^{29} residue to give, after regeneration, the title compound in high yield.

Treatment of porcine insulin (I) with 0.05 M CHD in 0.2 M borate buffer at 37°C for 12 h, yielded 1,2-dihydroxy-cyclohex-1,2-ylen (DHCH)-Arg-B^{22}-insulin complex (II) as the only product. Treatment of II with 0.5 M hydroxylamine at pH 7.0 at



PORCINE INSULIN (I)

DESCRIPTORS

Enzymes
trypsin, restricted action of on modified insulin (pig),

Pancreatic hormones
modified insulin (pig), preparation of,

Peptides, preparation
insulin (pig)
–, des-Ala-B^{30}, preparation of, modified reversibly on Arg-B^{22} by cyclohexane-1,2-dione,

37°C for 1 h, led to regeneration of I with unchanged biological activity. The tryptic incubation of the complex II at pH 8.0 and 37°C for 20 h, followed by fractionation of the digest on Sephadex G-50 column, gave des-Ala-B^{30}-DHCH-Arg-B^{22}-insulin complex (III) as the sole product. Treatment of III with hydroxylamine, followed by ultrafiltration and lyophilization, afforded (85% yield) des-Ala—B^{30}-insulin (IV) *(2-4)* which electrophoretic behaviour and amino acid composition were fully consistent with the structure proposed.

REFERENCES

1. L. Patthy and E. L. Smith, *J.Biol.Chem.* 250 (1975) 557.
2. L. J. Slobin and F. H. Carpenter, *Biochemistry* 5 (1966) 499.
3. J. Goldman and F. H. Carpenter, *Biochemistry* 13 (1974) 4566.
4. E. W. Schmitt and H.-G. Gattner, *Hoppe-Seyler's Z.Physiol.Chem.* 359 (1978) 799.

Abstractor: D. Keglević

DOCUMENTA CHEMICA YUGOSLAVICA

CROATICA CHEMICA ACTA

Croat. Chem. Acta Vol. **53** No. 1 1—114 A1—A12 C1—C10 (1980)

Zagreb, 5. svibnja 1980

SADRŽAJ

Opća i teorijska kemija

Kemijska sinteza

Analitička kemija

Biokemija

Prilozi

DOCUMENTA CHEMICA YUGOSLAVICA

CROATICA CHEMICA ACTA

Croat. Chem. Acta Vol. **53** No. 1 1—144 A1—A12 C1—C10 (1980)

Zagreb, May 5, 1980

CONTENTS

General and Theoretical Chemistry

Chemical Synthesis

Analytical Chemistry

Biochemistry

Appendix