CROATICA CHEMICA ACTA CCACAA **65** (3) 745–756 (1992)

ISSN 0011-1643
UDC 547.63
CCA—2093

Original Scientific Paper

Study of a Sterically Hindered Enol to Ketone Rearrangement by Stopped-Flow Gas Chromatography*[1]

*Lena Swahn and Per Ahlberg***

Department of Organic Chemistry, University of Göteborg, S-412 96, Göteborg, Sweden

and

*Zvi Rappoport***

Department of Organic Chemistry, The Hebrew University, Jerusalem 91904, Israel

Received December 02, 1991

A »stopped-flow« GLC method has been developed and applied for studying the rearrangement of the sterically hindered enol 1,1-dimesityl-3,3-dimethyl-1-buten-2-ol (**1**) to the ketone 1,1-dimesityl-3,3-dimethyl-2-butanone (**2**). The method is a three-stage technique using the gas chromatograph as both a chemical reactor and an analytical tool. Activation parameters have been estimated for the rearrangement and they indicate that this reaction is a catalyzed process rather than an uncatalyzed symmetry-forbidden reaction.

INTRODUCTION

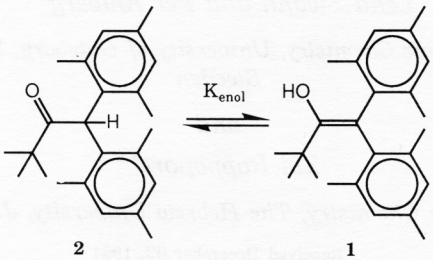
An uncatalyzed suprafacial [1,3] sigmatropic proton rearrangement is a symmetry-forbidden process according to the Woodward-Hoffmann rules.[2] Experimentally, such processes are unknown. The enol ⇌ ketone tautomerization reaction belongs to this class of reactions and indeed vinyl alcohol does not rearrange spontaneously and completely to acetaldehyde even at high temperatures in the gas phase.[3] Calculations at various levels show that the energy required for this reaction is high.[4] A theoretical estimate of the barrier (E_a) from the enol side is 67.2 kcal mol^{-1}.[5] The most recent high level calculated energy difference between vinyl alcohol and acetaldehyde indicate that the former is 11.1[6a] or 14.9[6b] kcal mol^{-1} more stable.

Three types of difficulties are encountered in an attempted experimental verification of the high barrier. First, simple enols are usually unavailable and when prepared by modern methods[7] they tend to ketonize. Second, due to the facile acid and base catalysis of the enol ⇌ keto interconversion, a catalyzed process by even small am-

* Dedicated to Professor Dionis E. Sunko on the occasion of his seventieth birthday.
** Author to whom correspondence should be addressed.

mounts of impurities will undoubtedly be much faster than the uncatalyzed process[8] and this seems to be the reason for the instability of the simple enols in solution. Third, even if the catalyzed processes will be excluded, competing reactions, such as cleavage of the keto and enol species may be of lower energy and hence faster than the enol ⇌ keto interconversion.

The availability of several crowded aryl-substituted simple enols[9] and their keto isomers as kinetically stable species enables their use in such studies. The kinetically stable enol 1,1-dimesityl-3,3-dimethyl-2-buten-2-ol (**1**) was chosen since it is easily isolated and stored, but it can be rearranged in hexane with CF_3COOH catalysis to its isomeric ketone 1,1-dimesityl-3,3-dimethyl-2-butanone (**2**).[10] The ketone **2** is more stable and the equilibrium constant, K_{enol}, (equation 1) in hexane at 80.6 °C is 0.006, thus making the reverse enolization reaction much slower than the ketonization.



2 **1** (1)

The **1** → **2** isomerization is relatively slow, presumably due to steric crowding. Both the initial state and more so the transition state of the ketonization are crowded.[11] An 'uncatalyzed' isomerization was therefore attempted, applying a working hypothesis that a 'normal' activation energy of <30 kcal mol^{-1}, will indicate a catalyzed process, whereas a much higher value may point to the occurrence of the forbidden uncatalyzed route. The activation entropy could presumably also distinguish between the alternatives since a small $|\Delta S^{\ddagger}|$ will fit an intramolecular process while a large negative $\Delta S^{\ddagger}$ is expected for a bimolecular catalyzed or intermolecular rearrangement.

A main obstacle in such experiment will be the conventional evaluation of activation energy from different experiments at different temperatures, since small differences in the amount of adventitious acid or base will give different extents of the catalyzed process. We therefore intended to determine the activation parameters by using the Varytemp method[12] which enables to evaluate the activation parameters in a simple kinetic experiment using continuous or stepwise variation of the temperature and measurements of the concentration of the sample at different reaction times. Additional advantages of this method are that it requires much less time and substrate and its accuracy is much better than that obtained by conventional procedures when reproducibility is a problem. The main advantage in our case is that the amount of (catalytic) impurities possibly remains constant at the various temperatures.

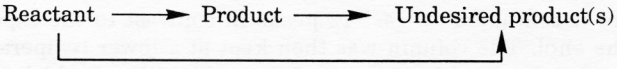
Unfortunately, this advantage cannot be applied since we encountered the third obstacle mentioned above, *i.e.* decomposition of the reacting species. During the search for a suitable analytical method to follow the reaction, we observed that while applying gas chromatography the enol reacted readily both in the injector port and during its migration on the column at temperatures above 160 °C. Two types of reactions were observed; the desired isomerization to the ketone and a competing undesired decom-

position. Both reactions were much slower at lower temperatures, enabling the separation of the enol, ketone, other reaction products, and impurities, at the cost of obtaining broader peaks.

Because of this behavior we have developed a three-step technique, involving two separation steps and one reaction step, to follow the kinetics by using the chromatographic column both as an analytical separation tool and as a reaction medium.

METHOD

Applications of the gas chromatographic column as a chemical reactor utilizing the continuous-flow technique in which a substrate is converted to products during its residence on the column by a simultaneous separation and reaction process have been reported.[13] Packed columns with a liquid phase on the solid support and a catalyst present were normally used. However, in contrast with the present method both the reaction and the separation stages usually occur simultaneously when the reactant passes through the column. Consequently, a broad peak is normally observed at a 'formal' retention time starting with that of the product and ending with that of the substrate if the former is more volatile, and *vice versa* if the latter is more volatile. This is a great disadvantage of the continuous-flow method since it is difficult to accurately estimate the peak areas. Another problem is that this technique is unsuitable for analyzing a reaction system which includes undesired reactions. Due to these difficulties we used a modified version of a stopped-flow technique, developed by Phillips and coworkers.[14] This method produces sharp peaks, is well suited for studies also of reactions when limited reactant material is available, and reactants may not have to be completely pure since trace impurities can be separated on the column. In addition, reversible reactions can often be studied since the efficient separation of the reactants and products enables simultaneous study of both the forward and the reverse reaction. The method also enables study of reactions that might involve product inhibition or autocatalysis. A special advantage is the ability to follow simultaneously the three reactions described in Scheme 1 where both reactant and product further lead to the same (usually undesired) product(s).



Scheme 1

Usually it is unknown if this undesired product is formed from the reactant, from the product of interest, or from both so that its formation complicates the kinetic study of the reactant → product reaction. In the present stopped-flow method, the 'undesired' species formed from each of the precursors is separately recorded, enabling to follow simultaneously the reactant → product, reactant → undesired product(s), and product → undesired product(s) reactions.

The analytical conditions are chosen so as to reduce as much as possible the extent of reaction during the separation stages when the enol and the reaction products migrate along the column. A sample of the enol is injected into a capillary column and separated from the initially present ketone and »impurities« at a moderately low tem-

perature. The carrier gas flow is then turned off and the temperature of the column is raised as to enable the separated substrates to react during an appropriate reaction time. Again, the enol undergoes both isomerization to the ketone and decomposition. The temperature is lowered sufficiently to reduce the rate of further reaction, the carrier gas flow is turned on, and the products of both reactions are again separated on the column. Due to this double stage procedure the chromatogram obtained at the end of this stage shows separate peaks for the ketone present originally and for the ketone formed on the column during the absence of gas flow (see Figure 1 below). This »stopped-flow« gas chromatographic method is applied at different temperatures and reaction times, and thus allows the calculation of the rate constant for the ketonization at several temperatures and the derived activation parameters.

Since the Varytemp method was not applicable in our system, we used this modified stopped-flow technique using capillary gas chromatography to estimate the activation parameters for the enol ⇌ keto reaction. The technique and its mechanistic implications are discussed below.

EXPERIMENTAL

General: The gas chromatography experiments were performed with a Varian GC 3400 equipped with a Varian autosampler 8000, and the data were collected and treated on a Varian computer DS 654. A 4 mm open glass insert was used in the splitless injector. The column used was a fused-silica capillary column of the type DB-5 (phenyl/methyl) with film thickness 0.25 μm. The column dimensions were 6 m × 0.25 mm. The carrier gas was helium and the flow rate approx. 2.7 mL/min.

Solvent and Materials: 1,1-Dimesityl-3-3-dimethyl-1-buten-2-ol (**1**) and 1,1-dimesityl-3,3-dimethyl-2-butanone (**2**) were prepared according to Nugiel and Rappoport.[10] Each of them was dissolved in hexane (FSA, HPLC-grade 95%) prior to analysis.

Design of Reaction Conditions and Analytical Conditions

In initial experiments to determine the enol purity a solution of the enol in hexane was injected into a 30 meter fused-silica capillary column and a high column and injector temperature (250 °C) was used in the gas chromatograph in order to obtain a rapid analysis. The resulting chromatogram was very complex showing insufficient separation and it contained at least 12 peaks in contrast to the expected two, for the ketone and the enol. The column was then kept at a lower temperature (160 °C) and a simpler chromatogram showing only five peaks, two of which due to initial impurities (see below) was obtained after a much longer (usually one hour) analysis time. We concluded that additional reactions to the ketonization, leading to a decomposition product **3**, are taking place at high temperatures (Scheme 2). For investigating the reactions of the enol inside the column we measured the amount of ketone and decomposition products generated during the time required for the GLC analysis under varying conditions such as injector and column temperature, and analysis time. A shorter, six meter column was used to speed up the analysis and also to decrease the amount of reaction while the enol is migrating on the column.

$$\mathbf{1} \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} \mathbf{2} \xrightarrow{k_{23}} \mathbf{3}$$

Scheme 2

An isothermal GLC analysis at 160 °C of the enol sample studied showed that it was ≥98.5% pure. The chromatogram displayed five peaks (Figure 1) which are, in order of increasing retention time: **3** – a decomposition product, **5** – am impurity, **1** – the enol, **2** – the ketone, and **4** – another impurity. The ketone peak (*ca.* 0.4%) in the enol sample was assigned by its identity with a ketone sample in a separate analysis.

Performance in the On-Column Reactions

The injection technique that we used was splitless sampling. For a splitless injection, the splitter is closed for a period of time (splitless delay time) while the sample is injected, vaporized, and transferred into the column.

The injector conditions affect the kinetic results since the enol is consumed at high injector temperature and/or long splitless delay time (*i.e.* the time at which the injector splitter valve is closed), and the amount remaining for rearrangement to ketone is decreased. Both the injector temperature and the splitless delay time affect the decomposition of the enol to **3** more than the rearrangement of **1** to **2**. We have studied this temperature and time dependence by varying injector temperature in the range of 190–250 °C and splitless delay time from zero to 30 seconds in order to optimize the injector conditions. For long splitless delay times, the sample remains in the injector until most of it is transferred into the column and therefore significant reactions can take place before the injector is purged. The temperature-dependence experiments showed that the formation of decomposition products (mostly **3**) was temperature dependent. On the other hand, very little ketone is formed in the injector under these circumstances. Consequently, in order to decrease the amount of reaction in the injector, a low injector temperature and short splitless delay time are necessary. However, a too low injector temperature gives insufficient vaporization of the sample and a short splitless delay time gives small peaks with an accompanying high integration error. For compensating the two effects we used an injector temperature of 210 °C and splitless delay time of 1.2 seconds for the following on-column rearrangements.

Attempts to neutralize the acidic sites on the column by injecting triethylamine together with the enol sample did not effect the rate of rearrangement of **1** to **2**. However, the rate of decomposition of **1** to **3** in the injector was increased fourfold and the rate of decomposition on the column was increased slightly.

A substantial decomposition took place on the column at high temperatures resulting in a large tailing of the **3**-peak and consecutive loss of enol during separation on the column. Too high temperature also affects the rearrangement of enol to ketone resulting in a valley between the enol and ketone peaks which no longer will be baseline separated. These studies help to define the best conditions for the analysis methods used for the kinetics. To obtain accurate kinetic data we performed a number of reactions with varying reaction temperatures and times but at the same analysis conditions. The column temperature was set to 160 °C, isothermal, which gave symmetrical peaks at a reasonable analysis time (14 minutes). At these conditions, good resolution was achieved and less then 0.5% of the enol was estimated to be consumed during analysis. The sample of enol was approx. 0.5 mM and the sample volume was 0.7 μL. The procedure for the stopped-flow reactions was as follows: The enol sample was injected and allowed to migrate on the column for 5 minutes which is a sufficient time to separate the enol **1** from the ketone **2** and the impurities by at least one meter. The carrier gas flow was shut off (takes about 3 seconds) and the temperature was raised (or lowered) to the desired rearrangement temperature (takes up to 2 minutes,

depending on the temperature). The purified enol was allowed to react, producing new ketone $\mathbf{2}_t$ and some decomposition $\mathbf{3}_t$ (the subscript*t* refers to the produced **2** and **3**, respectively, on the column after time *t*). After a certain amount of time (up to 40 minutes) the temperature was changed to the analysis temperature (takes up to 50 seconds) and the carrier gas flow was turned on for the separation and analysis stage. The outcome of this sequence of separation, reaction, and analysis is a chromatogram with seven peaks: **3**, **5**, $\mathbf{3}_t$, **1**, $\mathbf{2}_t$, **2** and **4** (Figure 1) in the order of increasing retention time. Corrections for reactions taking place during the heating and cooling of the column under stopped flow, whose extent is dependent on the time taken to reach the desired temperature, were introduced for each rearrangement temperature by measuring zero-points obtained on raising the temperature and directly lowering it again under stopped flow.

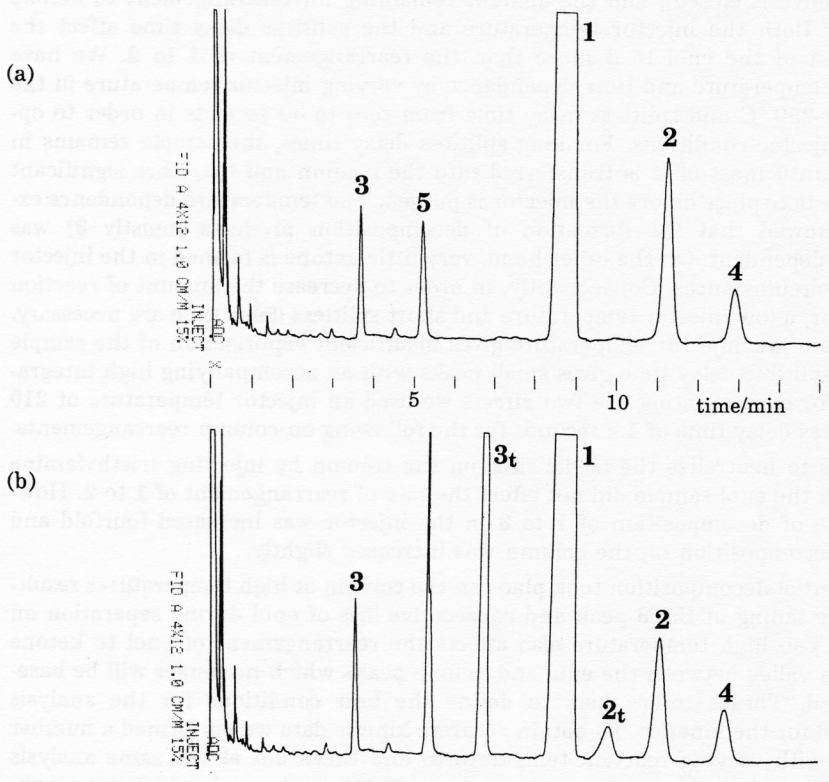


Figure 1. Chromatograms showing: (a) An isothermal analysis of the enol sample at 160 °C resulting in five peaks: **1** the enol, **2** the ketone, **3** the main decomposition product, **4** an unidentified impurity (used as reference), and **5** another impurity peak. (b) An analysis of the enol sample using the stopped-flow technique: The sample was separated for five minutes, the carrier gas was turned off, and the sample was allowed to react for 30 minutes. Thereafter the second separation stage was performed giving rise to the new peaks: $\mathbf{2}_t$ new ketone, and $\mathbf{3}_t$ new decomposition product. The peak appearing directly after carrier gas turn-on contains not only **5** but also some decomposition products.

The ketone sample: When the ketone was kept at 250 °C for 30 minutes the chromatogram showed only peaks for **2** and **4**. Neither **1** nor **3** were formed in the injector or on the column. Consequently, the rate constants in Scheme 2, for the proposed decomposition **2** → **3** (k_{23}) as well as for the **2** → **1** reaction (k_{21}) are negligible compared with k_{12} and k_{13}. We conclude that at our conditions the decomposition product **3** is formed only from the enol.

Kinetics

The enol undergoes both rearrangement to $\mathbf{2}_t$ and decomposition to $\mathbf{3}_t$. However, it is not possible to determine the rate constant, k_{12}, for the rearrangement by estimating the decrease in [**1**] since it is not only that **1** is consumed much faster than $\mathbf{2}_t$ is produced, but the **1** → $\mathbf{3}_t$ reaction rate seems to be of a higher order than the **1** → $\mathbf{2}_t$ process.

$$(3_t \xleftarrow{k_{13}}) \; 1 \xrightarrow{k_{12}} 2_t$$

However, if we use only the initial part of the reaction, when > 90% of **1** is still left after reaction, and ignore the production of **3**, to a first approximation, [**1**] could be taken as constant at every point in the kinetics and as we use **4** as an internal standard $[\mathbf{1}]_t \approx [\mathbf{1}]_0$ = constant × [**4**]. This constant was determined separately to be 146 from the 1/4 area ratio obtained from an ordinary analysis at a column temperature of 160 °C, isothermal, *i.e.* at continues flow. Therefore:

$$\mathrm{d}[\mathbf{2}]_t / \mathrm{d}t = k_{12}[\mathbf{1}]_0 = k'_{12} \times 146 \times [\mathbf{4}]$$

and after integration and rearrangement:

$$[\mathbf{2}]_t / (146 \times [\mathbf{4}]) = k_{12} \times t \; .$$

No calibration of the response of the detector to the concentrations was made and the ratio $[\mathbf{2}]_t/[\mathbf{4}]$ was assumed to be proportional to the ratio of the peak areas of $\mathbf{2}_t$ and **4**. A plot of $\mathbf{2}_t$(area)/(146 × **4**(area)) *versus* t should therefore be linear with a slope, k'_{12}.

Rearrangement has been performed at five column temperatures between 140 and 250 °C. The $\mathbf{2}_t$(area)/(146 × **4**(area)) *vs.* time plots are given in Figure 2 and the rate constants are collected in Table I.

TABLE I

First order rate constants derived from the plots in Figure 2.

Rearrangement temperature / °C	$10^6\ k'_{12}$ / s^{-1}
140	0.855
160	1.86
180	3.97
200	7.25
250	26.6

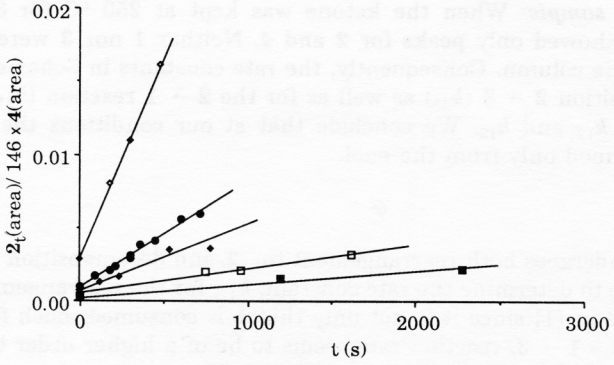
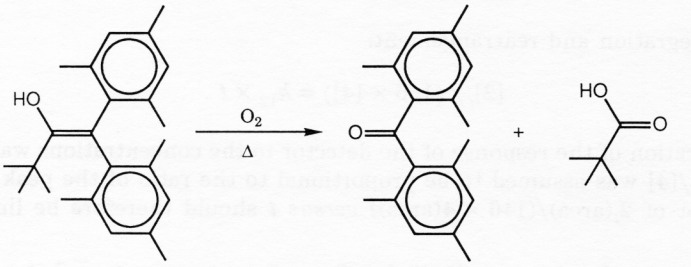


Figure 2. A plot of produced ketone (illustrated by the fraction $\mathbf{2}_t$(area)/(146 × **4**(area)) *vs.* rearrangement time for five different temperatures: ◇ at 250 °C, ● at 200 °C, ◆ at 180 °C, ◆ at 160 °C, and ■ at 140 °C.

RESULTS AND DISCUSSION

Identification of Impurities and Decomposition Products

Several arylsubstituted enols undergo oxidative cleavage and simultaneous isomerization to the ketones.[11,14] Consequently, when trying to identify the decomposition product **3** and the impurities **4** and **5**, a similar reaction was considered for **1**. A likely oxidation-cleavage reaction would lead to dimesityl ketone, **6**, and pivalic acid, **7** (equation 2).

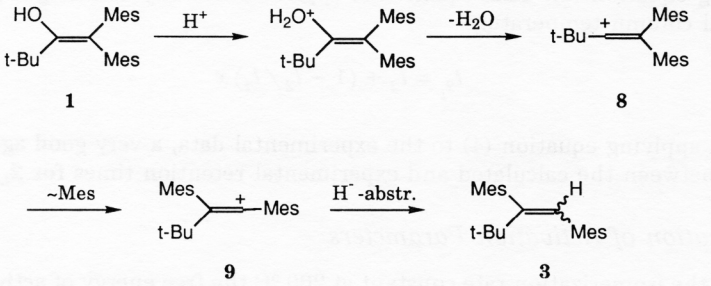


1 6 7 (2)

However, a GC analysis of authentic samples of **6** and **7** showed that none of them was identical with **3**, **4**, or **5**. Pivalic acid **7** has a much shorter and **6** has a somewhat shorter retention time than does **3** under our conditions. Also, none of these compounds could explain the observed mass spectrum of **3**.

Compound **3** is, as far as this study can tell, not an impurity in the enol or ketone samples but is a product of thermal reactions during the gas chromatographic analysis and/or photochemical reactions of the enol in solution. At very mild conditions **3** could not be detected in the enol sample whereas the ketone sample is free of **3** at all conditions so that **3** must be a decomposition product of the enol. The mass spectrum of **3** displayed the highest peak at *m/z* 320 (for **1** and **2**, m/z 336) and showed no peak at *m/z* 251, which is a characteristic peak of the fragment Mes_2CH^+. Consequently, either an oxygen or a CH_4 unit is lost. Although we performed no high resolution ex-

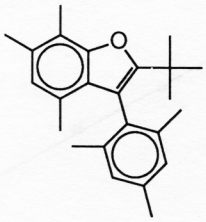
periment to distinguish these alternatives, we believe that the absence of the latest fragment or of a fragment at m/z 235 ($MesC^+(C_6H_3Me_2)$) indicates both that the oxygen is lost and that the two aromatic groups are no longer geminal. If the column is acidic enough to cause a heterolytic C–O bond cleavage to form the 2,2-dimesityl-1-*t*-butylvinyl cation **8** a β-mesityl migration[15] could take place to give the rearranged ion **9**. Abstraction of a hydride from the medium will account for the product formed (equation 3).[16]



(3)

Mes = mesityl

The amount of compound **5** seems to be constant when varying the analysis conditions so that the **1** → **5** reaction is not thermal. However, when a solution of the enol in carbon tetrachloride was exposed to light or is heated a clear increase in the amount of **5** was observed. However, when **1** was stored in other solvents (diethyl ether, benzene, or hexane) the concentration of **5** remains constant. The oxidative-cyclization of **1** to a substituted benzofuran was recently reported by Schmittel and Baumann[17] and we suspected that the latter may be one of the impurities **4** or **5**. When a sample obtained from Dr. Schmittel[18] was compared with **4** and **5** both its retention time and mass spectrum were identical with those of **5**, which was therefore assigned the benzofuran structure.



5

Compound **4** which was a minor component (<0.7%) of the mixture, has not yet been identified. It is an impurity which is apparently formed during the synthesis of the enol. It is the only compound that appears to be unaffected by reaction conditions and can therefore serve as an internal reference.

Identification of 2_t

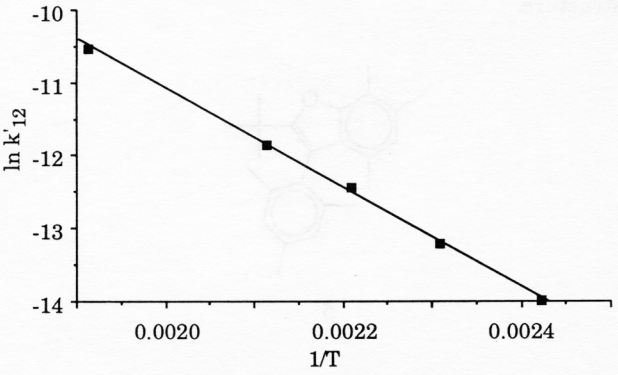
How do we ensure that the peak $\mathbf{2}_t$ formed between those for **1** and **2** is indeed that of the ketone **2** formed by rearrangement of the enol on the column? It is obvious that the retention time (t_{2_t}) for the new peak, $\mathbf{2}_t$, will be larger than that for **1** (t_1) but smaller than that for **2** (t_2) and that if the enol migrates at various times before its reaction then the formed ketone peak will appear at different retention times depending on the length of column left for the ketone to migrate on. It is possible to identify $\mathbf{2}_t$ by its retention time when we know t_{2_t}, t_1, and the initial separation time, x, by using equation (4). This equation is applicable for any carrier gas pressure and isothermal column temperature.

$$t_{2_t} = t_2 + (1 - t_2/t_1)\,x \tag{4}$$

When applying equation (4) to the experimental data, a very good agreement was obtained between the calculated and experimental retention times for $\mathbf{2}_t$.

Determination of Activation Parameters

From the isomerization rate constant at 200 °C the free energy of activation is $\Delta G^{\ddagger}$ = 39 kcal mol^{-1}. Since the $\Delta G^{\ddagger}$ for the [1,3] sigmatropic rearrangement must be equal or higher than the observed value, it is *at least* forty kilocalories per mole for the latter process. An Eyring ln k *vs.* $1/T$ plot of the kinetic data gives a straight line (Figure 3) with the slope corresponding to $\Delta H^{\ddagger}$ = 14 kcal mol^{-1}. The entropy of activation was calculated to be $\Delta S^{\ddagger}$ = −54 cal K^{-1} mol^{-1} at 200 °C. The linearity observed in Figure 3 suggests that the amount of catalytic impurities on the column is constant during the experiments, although the errors in the rate constants were not analyzed. The low activation enthalpy and the large negative activation entropy suggests that the process followed is not a suprafacial [1,3] sigmatropic uncatalyzed proton rearrangement, but the [1,3] proton rearrangement is probably non-concerted and is catalyzed by some species in the column liquid phase.



Contaminations in the Column[19]

The column used was a fused silica capillary column coated with a rather non polar stationary phase consisting of a crosslinked methyl phenylsiloxane. This phase belongs to the most uniform and stable stationary phase films available. Although fused-silica is generally considered to be inert it can exhibit undesirable surface activity in capillary column applications. Column surface activity can be ascribed to the silica surface structure and to impurities found in the surface monolayers of the glass. The fused-silica used in capillary columns is prepared synthetically from high purity silicon tetrachloride. The final product contains less than 1 ppm of metallic impurities, mostly alumina and iron. Various metallic oxides can act as Lewis acid sites. However, high quality fused-silica is essentially free of metallic impurities so it is unlikely that the surface composition could contain any Lewis acid sites. Another important structural detail of the silica surface is the hydroxyl groups attached to the surface silicon atoms. During heat treatment, surface hydroxyls condense to form siloxane bridges and water. The siloxane bridge can participate in a proton acceptor process with hydrogen bonding interactions. It has been shown that alcohol molecules can interact significantly with the siloxane surface by van der Waals interactions. If any of these medium components indeed catalyses the **1** → **2** reaction, our experiment indicates that it is not neutralized by added triethylamine.

CONCLUSIONS

The stopped-flow method developed here for studies of rearrangement reactions by using the gas liquid chromatograph as both chemical reactor and analytical tool is very convenient for probing specific problems and has some advantages compared with reactions in solution. One advantage is that a very small amount of material is needed as every kinetic point consumes only the amount of substrate required for one analysis. Another is that interferences from impurities are avoided as the substrate is first purified on the column. Moreover, the source of the impurities can be identified and their fate can be followed. In principle, by measuring and comparing few single point rate constants at increasing reaction percentage and times at different regions along the column a kinetic method for evaluating the homogeneity of the column could be developed. This is under study now. It shares with reactions in solution the disadvantage that the liquid phase could catalyze the reaction and it may have an additional undesired catalytic activity due to the column material. The medium in our experiment is defined but somewhat unconventional. The advantages of our stopped-flow method over the continuous-flow gas chromatographic reactor are its lower sensitivity to baseline fluctuations and the sharper peaks produced. The method is more efficient in eliminating the effects of any impurities than the continuous-flow method and it is preferable when more than the continuous-flow method and it is preferable when more than one signal-producing product is formed.

It is reasonable to conclude that the process followed is not a suprafacial [1,3] sigmatropic uncatalyzed proton rearrangement, but that the values measured relate to a catalyzed process, presumably by an acidic or a basic species present in the column liquid phase. Although our technique did not give the activation parameters for the uncatalyzed reaction but only a lower limit for its $\Delta G^{\ddagger}$ and $\Delta H^{\ddagger}$, the inherent features of the method could be used to attack this problem again either by using a purer enol **1**, by studying another system less prone to decomposition, by reducing the amount of catalytic impurities on the column, or by using a different liquid phase.

REFERENCES

1. Presented in part in the 10th IUPAC Conference on Physical Organic Chemistry, Haifa, August 5–10, 1990, Abstracts, p. 123.
2. (a) R. B. Woodward and R. Hoffmann, *The Conservation of Orbital Symmetry,* Verlag Chemie, GmbH Weinheim/Bergst., 1971, pp. 114-140, (b) C. W. Spangler, *Chem. Rev.* **76** (1976) 187.
3. (a) S. Saito, *Chem. Phys. Lett.* **42** (1976) 399. (b) S. Saito, *Pure Appl. Chem.* **50** (1978) 1239. (c) M. Rodler and A. Bauder, *J. Amer. Chem. Soc.* **106** (1984) 4025.
4. For a review on calculations regarding the rearrangement of vinyl alcohol to acetaldehyde see Y. Apeloig, in: *The Chemistry of Enols,* Z. Rappoport (Ed.), Wiley, Chichester, 1990, pp. 5-13.
5. W. R. Rodwell, W. J. Bouma, and L. Radom, *Int. J. Quantum Chem.* **18** (1980) 107.
6. (a) K. B. Wiberg, C. N. Breneman, and T. LePage, *J. Amer. Chem. Soc.* **112** (1990) 61, (b) Y. Apeloig, D. Arad, and Z. Rappoport, *J. Amer. Chem. Soc.* **112** (1990) 9131.
7. (a) B. Capon in Ref. 4, Chap. 5. (b) S. H. Bergens and B. Bosnich, *J. Amer. Chem. Soc.* **113** (1991) 958.
8. For a review on the kinetics of ketonization and enolization see J.R. Keeffe and A. J. Kresge, in Ref. 4, Chap. 7.
9. For review see (a) H. Hart, Z. Rappoport, and S. E. Biali, in Ref. 4, Chap. 8. (b) Z. Rappoport and S. E. Biali, *Acc. Chem. Res.* **21** (1988) 442.
10. D. A. Nugiel and Z. Rappoport, *J. Amer. Chem. Soc.* **107** (1985) 3669.
11. For an even more extreme case of steric hindrance to ketonization see E. B. Nadler and Z. Rappoport, *J. Org. Chem.* **55** (1990) 2673.
12. (a) P. Ahlberg, *Acta Chem. Scand.* **24** (1970) 1883. (b) S. Wold and P. Ahlberg, *Acta Chem. Scand.* **24** (1970) 618. (c) for comparison of the Varitemp and related methods see P. Ahlberg, *Chem. Scripta* **4** (1973) 41.
13. S. H. Langer and J. E. Patton, in: *New Developments in Gas Chromatography,* J. H. Purnell (Ed.), Wiley, New York, 1973, pp. 294-373.
14. C. S. G. Phillips, A. J. Hart-Davis, R. G. L. Saul, and J. Wormald, *J. Gas Chromatogr.* **5** (1967) 424.
15. For β-aryl rearrangements in vinyl cations see P. J. Stang, Z. Rappoport, M. Hanack, and L. R. Subramanian, *Vinyl Cations,* Academic Press, San Francisco, 1979, Chap. 6.
16. A m/z 320 peak was also observed in the reaction of **1** with thionyl chloride: E. Zipori and Z. Rappoport, submitted.
17. M. Schmittel and U. Baumann, *Angew. Chem., Int. Ed. Engl.* **29** (1990) 541.
18. We thank Dr. Schmittel for sending us this sample.
19. M. L. Lee, F. J. Yang, and K. D. Bartle, *Open Tubular Column Gas Chromatography. Theory and Practice,* Wiley, New York, 1984, pp. 51-59 and 73-81.

SAŽETAK

Primjena plinske kromatografije za proučavanje pregradnje sterički smetanih ketona metodom prekida protoka.

Lena Swahn, Per Ahlberg i Zvi Rappoport

Proučavana je pregradnja 1,1-dimestil-3,3-dimetil-1-buten-2-ola s pomoću originalno razvijene tehnike zaustavljenog protoka (stopped-flow) u plinskom kromatografu. Analizom izmjerenih aktivacijskih parametara zaključeno je da reakcija teče uz katalizu neidentificiranom komponentom iz tekuće faze u koloni.