8860 *J. Org. Chem.* **1996,** *61,* 8860−8865

Carbodications. 4.[1] Hydrogen Isotope Exchange of Crotonyl Cations in Superacid

Dan Fărcaşiu* and Ursula L. Bologa[2]

Department of Chemical and Petroleum Engineering, University of Pittsburgh, 1249 Benedum Hall, Pittsburgh, Pennsylvania 15213

Received May 14, 1996[⊗]

The title ion reacts in 1:1 DF−SbF_5 and exchanges up to five protium atoms with deuterium. The incorporation of label was measured by GC−MS analysis of the methyl crotonate formed by methanol quenching. The isotopomer distribution at about 60% conversion, which shows a minimum for the d_1 and a maximum for the d_4 species, indicates that the intermediate dication with the second charge at C(3) loses a proton faster from C(4) than from C(2). Formation of the pentadeuteriocrotonyl cation indicates that the 1,4-dication (acyl primary alkyl) or the 1,2-dication must intervene in the process. Computer modeling of the kinetics for the multiple exchange process to fit the experimental deuterium distribution allowed determination of the relative rate constants and isotope effects (KIEs) for the formation of the carbocations from alkenoyl cations (β-secondary KIE) and elimination from carbodications to alkenoyl cations (primary KIE). An exceptionally large β-secondary KIE of ca. 2.0/hydrogen was found for the formation of the dication. A small primary isotope effect of ca. 1.5 was found for elimination from the dications to the alkenoyl cations. Elimination from the 1,3-acylalkyl dication to form the nonconjugated 3-butenoyl cation is 6−7 times faster than elimination to the conjugated 2-butenoyl cation. The rate ratio for the conversion of 3-butenoyl cation to the 1,4-dication (primary alkyl cation) and 1,3-dication (secondary alkyl cation) is (0.025−0.030):1, whereas the relative rate of the formation of the 1,2-acylalkyl dication (the alternative route of achieving pentadeuteration) is zero.

Introduction

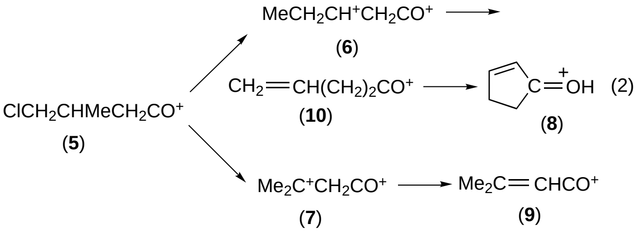
In connection with our work on the measurement of acid strength of strong acids and superacids,[3] our group has been investigating some reactions which exhibit acidity-dependent rates in such media. We reported earlier on the elimination of hydrogen chloride from the 4-chlorobutanoyl cation (**1**) in very strong superacids like 1:1 HF−SbF_5 (A) and 1:1 FSO_3H−SbF_5 (B), giving the 2-butenoyl (crotonyl) cation (**2**; eq 1).[4] Even though the

$$\underset{(\mathbf{1})}{\mathrm{Cl{-}(CH_2)_3{-}CO^+}} \rightarrow \underset{(\mathbf{3})}{\mathrm{{}^+CH_2{-}(CH_2)_2{-}CO^+}} \rightarrow \underset{(\mathbf{4})}{\mathrm{Me{-}CH^+{-}CH_2{-}CO^+}} \rightarrow \underset{(\mathbf{2})}{\mathrm{MeCH{=}CH{-}CO^+}} \quad (1)$$

reaction is in principle reversible, the equilibrium is fully displaced toward the right, indicating that the alkenoyl cation is much more stable than the 4-chloroacyl cation, as expected.

The elimination reaction was 15 times faster in the stronger[5] acid A than in acid B, and no reaction occurred in the relatively weak superacid 16:1 CF_3SO_3H−SbF_5. The reaction was, therefore, described as involving the ionization of **1**, with the formation of the acylalkyl dication **3**.[4,6] Fast rearrangement of **3** to the isomeric dication **4** and hydron loss lead to the product **2**. In a superacid of intermediate strength, 4:1 FSO_3H−SbF_5 (C),[5] however, the reaction is 1.3 times faster than in acid B, indicating that a base-catalyzed mechanistic component adds to the process of eq 1 in that particular solution.[4]

The relative stability of the doubly charged ions **3** and **4** is determined by the distance between the two charges, favoring **3**, and the degree of substitution of the alkyl cation site, favoring **4**. If **3** were highly unstable relative to **4**, the hydrogen shift could be concerted with ionization, **1** going directly to **4**. To help discern between the two mechanistic possibilities, we studied the reaction of the branched homolog of **1**, 4-chloro-3-methylbutanoyl cation (**5**).[7] In this case the initial 1,4-dication (primary[8]) rearranges competitively to one of two 1,3-dications: the secondary ion **6** and the tertiary ion **7** (eq 2). For the concerted mechanism, it is expected that the more stable



---

* Corresponding author: tel, 412-624-7449; fax, 412-624-9639; e-mail, dfarca@vms.cis.pitt.edu.

[⊗] Abstract published in *Advance ACS Abstracts,* December 1, 1996.

(1) For the previous paper in the series, see: Fărcaşiu, D.; Ghenciu, A. *J. Org. Chem.* **1991**, *56*, 6050.

(2) On leave during 1993 from the Organic Chemistry Department, Polytechnic University of Bucharest, Romania.

(3) (a) Fărcaşiu, D.; Marino, G.; Miller, G.; Kastrup, R. V. *J. Am. Chem. Soc.* **1989**, *111*, 7210 and previous papers cited therein. (b) Fărcaşiu, D.; Miller, G.; Ghenciu, A. *J. Catal.* **1992**, *134*, 118. (c) Fărcaşiu, D.; Ghenciu, A. *Ibid.* **1992**, *134*, 126. (d) Fărcaşiu, D.; Ghenciu, A. *J. Am. Chem. Soc.* **1993**, *115*, 10901. (e) Fărcaşiu, D., Li, J. Q. *J. Phys. Chem.* **1994**, *98*, 6893. (f) Fărcaşiu, D.; Li, J. *J. Catal.* **1995**, *152*, 198.

(4) Fărcaşiu, D.; Miller, G. *J. Org. Chem.* **1989**, *54*, 5423.

(5) From kinetic measurements, a rough estimation of relative strength A/B/(5:1 FSO_3H−SbF_5) of (>5000):1:10^{-4} was made; see: Brouwer, D. M.; van Doorn, J. A. *Recl. Trav. Chim. Pays-Bas* **1970**, *89*, 553; **1972**, *91*, 895.

(6) For the analogous HCl elimination converting a 3-chloroalkyl cation to an alkenyl cation, see: Fărcaşiu, D.; Rich, R.; Rose, K. D. *J. Org. Chem.* **1989**, *54*, 4582 and earlier work cited there.

(7) Fărcaşiu, D.; Miller, G.; Sharma, S. *J. Phys. Org. Chem.* **1990**, *3*, 639.

S0022-3263(96)00889-4 CCC: $12.00 © 1996 American Chemical Society

7 be formed in much greater amount than **6**, but in reality, the product of methyl migration (**5** → **6**), hydronated cyclopent-2-enone (**8**), and the product of hydrogen migration, (**5** → **7**), 3-methylbut-2-enoyl cation (**9**), were obtained in similar quantities. (Formation of the cyclic product **8** was rationalized as involving conversion of **6** to the pent-4-enoyl cation (**10**) followed by intramolecular acylation. An analogy existed in the conversion of the 1,3-dimethylallyl cation to the hydronated 2-methylcyclopentenone by reaction with carbon monoxide.[9]) This result supported the mechanism of eq 1, in which ionization and migration take place in separate, consecutive steps, the first being rate-determining, the second fast and nonselective.[7]

It seemed also conceivable that the process be concerted and the pathway be determined not only by the stability of the intermediate, **6** or **7**, but also by the conformation of the reactant (**5**) in which ionization takes place; the rotamer forming **7** is more sterically crowded than the one forming **6**. This reasoning, however, contravenes the Curtin–Hammett principle.[10]

The reaction pathway from **6** to **10** could consist of a hydride shift, the driving force of which is the repulsion between the two positive charges followed by hydron loss. Alternatively, a succession of elimination from C(4), hydron addition, and elimination from C(5) accomplishes the same transformation. Reaction of **5** in deuterated acid B (1:1 FSO_3D–SbF_5), which gave ketone **8** containing deuterium in the CH_2 groups, offered proof for the second alternative.[7]

We have now secured a quantitative description of formation of acylalkyl dications and of the various hydron loss and readdition processes possible for such species, from the study of the isotope exchange occurring when cation **2** reacts in a deuterated superacid for longer time. The study has revealed new and unexpected reactivity patterns, relative rates for formation of and proton loss from acylalkyl dications, and unprecedented values for isotope effects in the formation and reactions of carbocations, resulting fom the presence of a second charge nearby.

Experimental Section

Materials and Methods. Antimony pentafluoride (Ozark Mahoning) was redistilled at atmospheric pressure under nitrogen, in a drybox. Deuterium fluoride (99%-*d*) was procured from Cambridge Isotope Laboratories, in a Monel cylinder. Crotonyl chloride (Aldrich; 90%) was redistilled at atmospheric pressure. For purity evaluation, a sample of the distilled material was converted to its methyl ester.[11] GLC analysis of the crude ester showed a purity of 96%. The other chemicals were commercial A.R. grade materials and used as purchased.

NMR spectra of HF(DF)-containing solutions were run in Kel-F tubes[12] manufactured in the following way: A 5.5 mm diameter flat-bottomed hole, 214 mm in length, was precision-drilled into a 220 mm long Kel-F rod. The outer diameter of the tube was obtained by reducing the rod as follows: 8 mm o.d. for a length of 46 mm from the closed end; 9 mm o.d. (which fits inside a precision, thin-walled 10 mm glass NMR tube) for a length of 100 mm; 8 mm o.d. for 54 mm; 15 mm o.d. for a length of 20 mm. The closed end was rounded on the outside to fit the inner curvature of the 10 mm glass NMR tube, and a deep thread was cut for a length of 15 mm at the open end. A 12 mm diameter groove was cut in the flat surface at the open end, to fit a Teflon–PTFE O-ring. A longitudinal slit, less than 0.5 mm deep, was cut in the outer wall of the 9 mm o.d. section of the tube. A screw cap, 21 mm o.d. and 17 mm total height, with a flat end 4 mm thick and an inner thread fitting the thread of the tube, was also made from Kel-F; it provides a good seal with the O-ring. The space remaining between the Kel-F and glass tubes at the bottom serves as a chamber for the lock solvent, placed in the glass tube. When the Kel-F tube is slid into the glass tube, the air and some excess lock solvent move through the longitudinal slit to the upper chamber. Some Teflon tape may be wound around the Kel-F tube about the point where the glass tube ends to reduce the evaporation of the lock solvent, which is low even without this precaution.

Deuterium NMR spectra (run at 46.073 MHz)[13] and GC–MS analyses[14] were conducted as described previously.

Deuteriofluoroantimonic Acid. Freshly distilled antimony pentafluoride (50 g) was placed in a Teflon–FEP bottle inside a drybox filled with nitrogen. The Monel cylinder containing 10 g of deuterium fluoride was cooled in dry ice, inverted, and emptied into the same Teflon bottle, also cooled. The bottle was capped, allowed to come to room temperature with constant swirling, and reweighed. The amount of DF introduced was 9.4 g. Addition of more SbF_5 (51.9 g) gave the DF–SbF_5 (0.95:1) mixture.

D–H Exchange in the Crotonyl Cation (2). DF–SbF_5 (2 mL) was placed in an NMR Kel-F tube cooled in dry ice, inside the drybox. Crotonyl chloride (0.275 mL, 0.300 g) was added with a micropipet to give a solution in which the ratio DF:**2** was approximately 7.5:1. The tube was capped, shaken, and then brought to room temperature and out of the drybox. It exhibited the right protium and ^{13}C NMR spectra.[4] The sample was placed in an oil bath maintained at 60 ± 1 °C, and the progress of the reaction was ascertained from the decrease of the acid peak and increase of the C–D peaks in the ^2H NMR spectrum taken after increasing times of warming. The reaction was terminated by reaction with methanol in pentane at low temperature followed by washing and drying the methyl ester solution thus obtained, as described in detail earlier.[6] The deuterium content of the methyl crotonate was determined by GC–MS analysis.

Results and Discussion

Deuterium Distribution in the Product. Monitoring the reaction of cation **2** in deuterated acid A at 60 °C by ^2H NMR indicated that protium–deuterium exchange occurred at all three carbons and the extent of deuteration varied in the order Me > Cα > Cβ. A spectrum taken after 154 h of reaction is shown in Figure 1 in the Supporting Information. The integration was not accurate, especially for the Cβ-D signal, which is not well separated from the signal of the D_3O^+ impurity; the ratio of the Cα-D signal to the CD_xH_{3-x} signal is roughly 1:4.8. The ratio of the Cα-D signal to the CD_xH_{3-x} signal in the ^2H NMR was lower than 1:3 throughout the reaction.

For a more accurate determination, the reaction was quenched in methanol (eq 3)[6] and the resulting methyl but-2-enoate (crotonate, **11**) was analyzed by GC–MS.

$$\mathbf{2} + \mathrm{MeOH} \rightarrow \underset{\mathbf{11}}{\mathrm{Me{-}CH{=}CH{-}COOMe}} \qquad (3)$$

---

(8) A kinetic study like this cannot elucidate the actual structure of primary alkylacyl dications (e.g., **3**) written here in the conventional representation; we feel that at this stage only theoretical calculations can address such a problem.

(9) Hogeveen, H.; Gaasbeek, C. J. *Recl. Trav. Chim. Pays-Bas* **1970**, *89*, 395.

(10) Curtin, D. Y. *Rec. Chem. Prog.* **1954**, *15*, 111.

(11) Furniss, B. S.; Hannaford, A. J.; Rogers, V.; Smith, P. W. G.; Tatchell, A. R. *Vogel's Textbook of Practical Organic Chemistry*, 4th ed.; Longmans Scientific-John Wiley: New York, 1978; p 512.

(12) Fărcaşiu, D. *J. Org. Chem.* **1979**, *44*, 2103.

(13) Kogelbauer, A.; Reddick, J.; Fărcaşiu, D. *J. Mol. Catal.* **1995**, *103*, 31.

(14) Fărcaşiu, D.; Ghenciu, A.; Li, J. Q. *J. Catal.* **1996**, *158*, 116.

Table 1. Measured and Calculated Distribution of Deuterium in 2 after Exchange

ion	found[a]	calculated[b,c]
2-d_0	38.3	38.2
2-d_1	3.2	4.5
2-d_2	8.3	7.4
2-d_3	16.8	16.7
2-d_4	22.8	22.8
2-d_5	10.6	10.5

[a] Estimated uncertainty 1−2%. [b] The parameters used in optimization (with the final value in parentheses) were $Q = k_b{:}k_{-a}$ (6.22); $L = k_c{:}k_{-b}$ (0.0286); $J = k_d{:}k_a$ (0.0); P = primary isotope effect for $>CH(D)-C^+< \rightarrow >C{=}C<$ (1.480); $1/B$ = β-secondary KIE for formation of $>CH(D)-C^+<$ from $-CH(D){=}C<$ or $>CH(D)-C{=}C<$ (1.995). The rate constants (k_i) are defined in Schemes 1 and 2. [c] Calculated deuterium content ratios $C\beta$-D:$C\alpha$-D:CD_xH_{3-x} = 0.44:1.00:3.95.

It was immediately apparent that multiple deuteration of **2** had taken place, with the predominant formation of tri- and tetradeuterated material; this observation was confirmed in duplicate experiments. It was also apparent that significant fractionation occurred along the GLC column, the heavier (more deuterated) species eluting faster. A spectrum taken at the middle of the GLC peak is a reasonable representation of the isotopomer composition and is shown for illustration in Figure 2 in the Supporting Information.

For quantitative analysis, the ester obtained by quenching the reaction of Figure 1 was subjected to GC−MS, taking 36 spectra at 1.05 s intervals during the elution of the peak of **11**. The first spectrum gave a distribution of 46.3% d_4 and 53.7% d_5, whereas the last five spectra gave 100% d_0. The distribution of isotopomers in the product was obtained by summing up the 36 mass spectra. The result, after correction for the natural C-13 content, is shown in Table 1.

The multiple deuteration occurring in **2** indicates that elimination from C(4) of dication **4**, giving the nonconjugated but-3-enoyl cation (**12**), takes place. Deuteronation of the latter leads to the incorporation of label in the methyl group of **2**. Alternatively, deuteration of the methyl group could be achieved by base-catalyzed conversion of **4** to vinyl ketene (**13**) and deuteronation of the latter. Ketenes were reported as intermediates in reactions of carboxylic acids in fuming sulfuric acid.[15] Their intermediacy was assessed as unlikely for the reaction of the chloroacyl cation **1**,[4] but for completeness of discussion we have to consider it here as well. The reaction graph depicting all species formed by hydron additions and eliminations starting with cation **2**, including primary carbocations (**3** and **14**) and a dication with the charges at adjacent carbon atoms (**15**), is shown in Scheme 1.

A remarkable feature of the results is that the isotopomer distribution (Table 1) shows a minimum for the monodeuterated species (**2**-d_1) and a maximum for the tetradeuterated species (**2**-d_4), when a sizable amount of unreacted material (38% **2**-d_0) still exists. This result is hard to reconcile with the intermediacy of **13**, for which the first three deuterium atoms are exchanged into the methyl group by the same reaction, namely, proton loss to **13** and deuteronation back to **2**. Inasmuch as these three steps occur with the same specific rate, at the 62% conversion of the starting material, **2**-d_1 should be the main product, present in roughly the same amount as the remaining **2**-d_0, and the content of d_3 would be in the range of 6−8%. As a matter of fact, the statistical factor makes the second deuteration slower than the first and the third slower than the second, skewing even more the isotope distribution in the favor of **2**-d_1. Moreover, the fourth deuteration would occur by another reaction than the first three; the predominance of the d_4 species in the product would require that **13** → **12** be much faster than **13** → **2**, a requirement incompatible with the ratio higher than 3:1 of the deuterium concentrations in the methyl group and at Cα observed by ^{2}H NMR. This analysis eliminates the intermediacy of **13** from consideration. The observed isotopomer distribution indicates that the d_1−d_4 species must be formed by consecutive, rather than competitive, pathways and is thus compatible only with the mechanism involving the dication **4** as intermediate. It also requires that in the reaction of **4**, elimination from C(4), giving **12**, be faster than elimination from C(2), regenerating **2**.

Another notable feature of the experimental results shown in Table 1 is the existence among the reaction products of the pentadeuterated ester, indicating that all hydrogen atoms in **2** are exchangeable. This finding shows that **4** is not the only carbodication intermediate in the process. In addition to it, the acyl primary alkyl dication **3** or the isomer with the alkyl cationic center α to the acyl cation center (**15**), or both, must intervene in the process. The hydrogen−deuterium exchange is, therefore, described by the equations of Scheme 2. The scheme represents a contracted description of the process. Thus, all ions **12** can react to give the respective dications **3**, in the manner shown for **12**-*2-d*, although for species **12**-*2,3-d*$_2$, **12**-*2,3,4-d*$_3$, and **12**-*2,3,4,4-d*$_4$, this pathway represents a "dead end". Likewise, each dication **4** can lose a deuteron in competition with the loss of a proton, in the manner shown in the scheme for **4**-*2,3,4,4-d*$_4$. This reaction reverts **4**-*2-d* to unlabeled **2**, **4**-*2,4-d*$_2$ to **2**-*4-d*, etc.

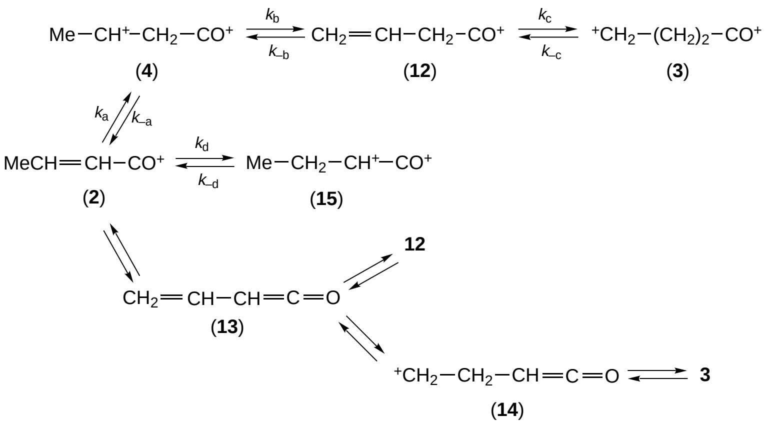
Kinetic Analysis. For modeling the kinetics of the H/D exchange process, the further reactions of the product ions **2** in Scheme 2 must be considered as well. The reaction graph becomes, therefore, rather complicated. Its level of complexity is determined by the fact that deuterated species differ by both the number and the position of deuterium atoms. Thus, there are three species identified as **2**-d_1, four species identified as **2**-d_2, etc. The total number of ions in the expanded graph is 69, but only the 16 ions **2**-d_0 to **2**-d_5 are counted as starting materials and products and only the sums of species with the same level of deuteration are measured. Because all the reactions which form the carbocations obey the same kinetic law, it can be seen immediately that the distribution of deuterium in **2** (and **11**) after reaction, that is, the ratios $d_0{:}d_1{:}d_2{:}d_3{:}d_4{:}d_5$, is determined by the rate constant ratios $k_b{:}k_{-a}$ (Q), $k_c{:}k_{-b}$ (L), and $k_d{:}k_a$ (J) and also by the primary isotope effects for the conversions of carbocations to alkenes (rate of $>CH-C^+<$ over rate of $>CD\text{-}C^+<$) and the secondary isotope effects for the conversion of alkenes to carbocations.[16] The α-secondary isotope effect should be negligible because the hybridization of the reacting center is the same in reactant and product. A list of the parameters necessary for the kinetic analysis is given in footnote *b* of Table 1.

---

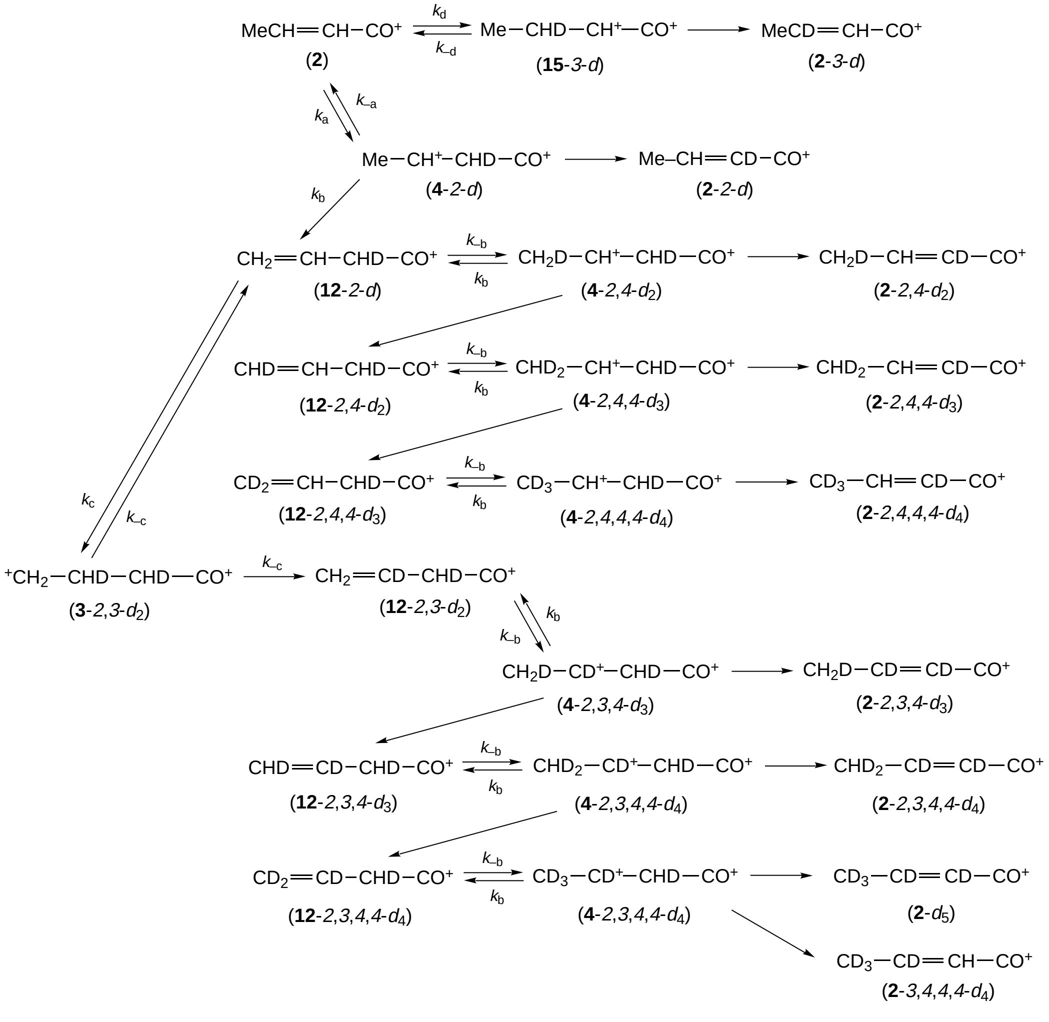
(15) Ogata, Y.; Harada, T.; Sugimoto, T. *Can. J. Chem.* **1977**, *55*, 1268.

(16) Collins, C. J., Bowman, N. S., Eds. *Isotope Effects in Chemical Reactions*; Van Nostrand-Reinhold: New York, 1970.

Scheme 1



Scheme 2



Considering that the ions **2** are the only species observable in solution, it follows that not only the dications but also the β,γ-alkenoyl cations **12** can be treated as unstable intermediates. Thus, for an infinitessimal degree of conversion of **2**, the distribution of the products is determined by the parameters Q, L, and J and by the isotope effects. At the same time, the degree of conversion of the isotopomers of **2** (**2**-d_1 to **2**-d_4) is equal to that of the parent multiplied by the secondary isotope effect, when applicable. It is likely that the values for the β-secondary KIEs are different for the formation of the three dications, **3**, **4**, and **15**. It can be seen, however, that all dications in the reaction scheme have at least one β-deuterium atom; therefore, the KIE is effective starting with the second β-deuterium atom present. At the same time, the ions **3** and **15** with two β-deuterium atoms can only revert to their progenitors, which means that they are mechanistic "dead ends". Consequently, only the formation of **4** (from either **2** or **12**) is affected by a β secondary KIE.[17] The number of unknown

---

[17] V. J. Shiner, Jr., in ref 16, pp 90−159, especially pp 129−131, has indicated that β-KIE is higher for the heavy isotope in a methylene group than in a methyl group. The difference does not seem large enough, however, to warrant using here two values for this parameter instead of one. The value found should be considered as an average between the two.

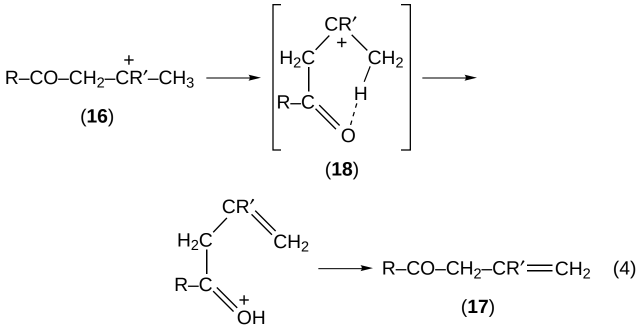
variables can be reduced even further, considering that all eliminations from isotopomers of **15** to isotopomers of **2** are equally affected by a primary isotope effect, so the latter can be incorporated in the relative rate J. As the results below indicate, its value would be irrelevant, anyway.

It can be seen that there are six unknown parameters, Q, L, J, β-KIE, and primary KIEs, for elimination from ions **3** and **4**, respectively (this holds if the two primary isotope effects are different, otherwise the number of unknowns reduces to five). The isotope effect in the reaction of **4** has a much greater effect than the isotope effect in the reaction of **3** because eliminations from **4** play a much greater part in the overall process than elimination from **3**. At the same time, there are five measured quantities, the concentrations of **2**-d_1, -d_2, -d_3, -d_4, and -d_5 at a given level of conversion. The quantity of **2**-d_0 is not an independent variable, but it is the measure of the degree of conversion.

An approximate solution to the kinetics of exchange can be obtained taking very small but finite levels of conversions of **2** in each step and updating the concentrations of all components (**2**−**2**-d_5) at the end of each step, to be used as input for the next step. The calculation is then repeated, giving different values to the kinetic parameters, until the predicted isotopomer concentrations match the measured values. A computer program, shown in the Supporting Information, was written to conduct this calculation. It was used to calculate the product distribution for arbitrarily chosen values of the parameters, varying the latter until the best fit (by the least-squares method) with the experimental results was obtained. To simplify the calculations (because no optimization program was available, the parameters were varied by typing in the new values for each calculations), the same value for the primary isotope effect for elimination from ions **3** and **4** was taken (denoted as P). The initial guess for the primary KIE could be anywhere between 2 and 9,[16] with the most likely range between 4 and 7.[16,18] For the β-secondary KIE, values between 1.05 and 1.33 have been reported,[17,19] with the value reported to increase as the demand for electrons by the carbocationic center increases.[19] This quantity was expressed in the computer program by a parameter B, defined as β-KIEA = $1/B$. The examination of data indicates that parameter Q has to be greater than 1, and general considerations suggest that J and L, measuring the formation of a dication with adjacent charges and of a primary alkyl, acyl dication, respectively, are most likely small numbers. The parameters P and $1/B$ were held to be greater than 1; the limiting values of 8.0 and 1.05 were used as initial values in one series of calculations. The conversion per step was 0.0033, which is 0.33% of the still unreacted **2** (**2**-d_0). A few calculations with a conversion per step of 0.0015 gave results essentially identical with those of the calculations with a 0.0033 fractional conversion per step.

The first result of the calculations was that for any combination of the other parameters the best fit resulted for $J = 0$. This indicates that the pathway involving dication **15**, with adjacent charges, does not intervene in the process. Another observation was that values for the isotope effects within the "most probable" range give a very poor fit. Variation of the four non-zero parameters gave at first a rapidly improving fit, but then a rather flat area was reached for values of L between 0.025 and 0.030, Q between 6 and 7, $1/B$ around 2.0, and P around 1.5. The calculated product distribution for $L = 0.0286$, $Q = 6.22$, $P = 1.480$, and $1/B = 1.995$ is shown in Table 1. A few calculations run with different values of the primary isotope effect for elimination from ions **4** (*P1)* and **3** (*P2*) indicated that the two quantities do not differ much, but *P2* seems to be the smaller of the two.

Discussion. The results of kinetic modeling show that the kinetic preference for β,γ-elimination over α,β-elimination from **4** ($Q = 6-7$) is significant. Considering the statistical factor (three γ-hydrogens and two α-hydrogens in **4**) formation of **12** is faster than formation of **2** by a factor of 10. Formation of the less stable, nonconjugated isomer under kinetic control was reported for the hydron loss from the β-acyl carbocation intermediates of Friedel−Crafts acylation of alkenes **16** (eq 4),



which gives β,γ-unsaturated ketones **17**. This observation was rationalized by the intervention of a cyclic transition state for elimination (**18**), in which the carbonyl oxygen acts as the base.[20] We see now in the case of the acylalkyl dication **4** that the nonconjugated alkenoyl cation **12** is the kinetically controlled elimination product, even though a cyclic transition state cannot intervene in this case.

Formation of the dication **3** from **12** is retarded relative to the formation of the isomer **4** by a factor of 30−40. This is a very small retardation for a primary cation relative to a secondary cation; a similar rate ratio, about 20, was found between superacid-catalyzed elimination of HCl from 3-chlorobutanoyl cation and from 4-chlorobutanoyl cation.[21] There are no other unambiguous examples of such a competition to offer a term of comparison for these numbers. An idea can be formed from the comparison of secondary and tertiary carbocations; thus, in the reaction of alkenes with trifluoroacetic acid, the rate ratio for the formation of a secondary carbocation and a tertiary carbocation was close to $1{:}10^5$.[18] The charge repulsion, much greater for the 1,3-dication than for the 1,4-dication, is responsible for the reduced rate ratio found in the reaction of the alkenoyl cation **12**.

The value of the primary isotope effect (P) is small but not unprecedented. In an extreme case, it was found that

---

[18] Fărcaşiu, D.; Marino, G.; Hsu, C. S. *J. Org. Chem.* **1994**, *59*, 163.

[19] (a) Creary, X. *J. Org. Chem.* **1976**, *41*, 3740. (b) Sunko, D. E.; Szele, I.; Tomic, M. *Tetrahedron Lett.* **1972**, 1827. (c) Gassman, P. G.; Pascone, J. M. *J. Am. Chem. Soc.* **1973**, *95*, 7801.

[20] (a) Praill, P. F. G.; Saville, B. *Chem. Ind. (London)* **1960**, 495. (b) Praill, P. F. G. *Acylation Reactions: Their Applications and Mechanisms*; Pergamon Press: Oxford, 1963.

[21] (a) Fărcaşiu, D.; Miller, G. Unpublished. (b) Miller, G. Ph.D. *Thesis*, Clarkson University, 1991.

[22] Heck, A. J. R.; de Koning, L. J.; Nibbering, N. M. M. *J. Am. Soc. Mass. Spectrom.* **1991**, *2*, 453.

hydron transfer from the CH_5^+ cation to ammonia in the gas phase has no kinetic isotope effect ($k_H/k_D = 1$).[22] The low value which we found in our case may indicate that the position of the transition state for the elimination is far removed from the midpoint of the transfer of proton/deuteron.[23] On the other hand, the value obtained for the β-KIE (1/B) of 2/hydrogen atom is unprecedented. The direction of change (greater value for the less stable cationic species) is as expected,[19] but the magnitude indicates an enormous demand for hyperconjugative stabilization by the β-hydrogen in the formation of the dication.[17,19]

Acknowledgment. Financial support was provided by NSF (Grant No. CTS 9528412). Support was also obtained from NSF for the purchase of the DMX300 NMR instrument (Grant No. 9413698). Mr. William Gollatz helped with writing the computer program.

Supporting Information Available: ^{2}H NMR (Figure 1) and GC−MS (Figure 2) spectra and the computer program for kinetic analysis (14 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

JO960889V

---

[23] (a) Westheimer, F. H. *Chem. Rev.* **1961**, *61*, 265. (b) Melander, L. *Isotope Effects on Reaction Rates*; Ronald Press: New York, 1969; pp 24−32. (c) Willi, A. V.; Wolfsberg, M. *Chem. Ind.* **1964**, 2097. (d) Bender, M. L. *Mechanism of Homogeneous Catalysis from Protons to Proteins*; Wiley-Interscience: New York, 1971; Chapter 4.