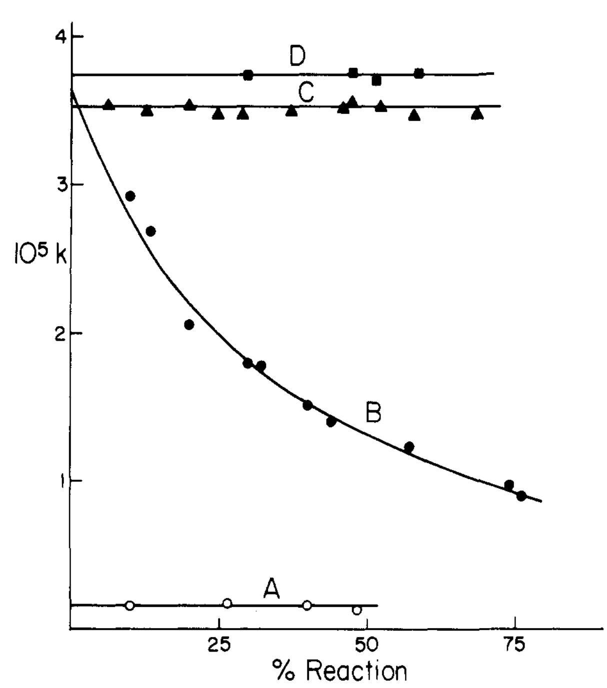
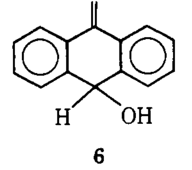


Figure 1. Change of the integrated first-order constants k_t and k_α with the progress of the reaction of 0.002 M **2** in the presence of 0.004 M 2,6-lutidine in TFE at 49.6 °C: A, k_t in the presence of 0.0092 M Bu_4NBr; B, k_t without added Br^-; C, k_α without added Br^-; D, k_α in the presence of 0.01 M Bu_4NBr.

9-Anisoylanthracene (**5**) is formed at higher reaction temperature.

The loss of optical activity is a first-order process, both in the absence (line C) and in the presence (line D) of 0.01 M Bu_4NBr. The $10^5\ k_\alpha$ values are 3.57 and 3.71 s^{-1}, respectively, almost identical with $k_t{}^0$.

Loss of optical activity by a rate-determining ionization of the secondary hydroxy group (route B, Scheme I) is excluded for three reasons: (i) by the fit of the experimental points to line B which was calculated by using $k_t{}^0$ and α for the bromide ionization model; (ii) by the similarity of $k_t{}^0$ for **2** and for **1** ($k_t{}^0(\mathbf{1}) = 1.08 \times 10^{-5}\ s^{-1}$ in TFE at 35 °C[15]); (iii) since the rate constant for the rearrangement of the hydrogen analogue **6** to a 9-substituted anthracene, which presumably proceeds via an initial ionization of the hydroxy group to the ion **7**, is $k_{rear} = 8.75 \times 10^{-6}\ s^{-1}$, i.e., ~4 times lower than $k_t{}^0$ for **2**.[16]



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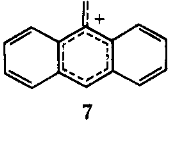

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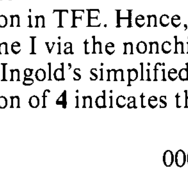

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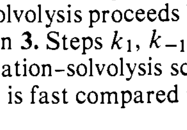

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The extent of common ion rate depression, together with the identity of $k_t{}^0$ and k_α within the experimental error,[17] excludes both product formation from ion pairs and ion-pair return with racemization in TFE. Hence, the solvolysis proceeds by route A of Scheme I via the nonchiral ion **3**. Steps k_1, k_{-1}, and k_2 amount to Ingold's simplified ionization-solvolysis scheme.[6a] The isolation of **4** indicates that k_3 is fast compared with the rate of formation of the vinylic solvolysis product.

The present work confirms the applicability of the k_α-k_t probe for evaluating the extent of ion-pair return in vinylic solvolysis. The results agree with previous results that ion-pair return in α-arylvinyl cations is not very extensive in moderate to good ionizing solvents.[18]

If a similar behavior would be observed for other 9-(α-bromo-*p*-substituted arylidene)-10-hydroxy-9,10-dihydroanthracenes, a comparison of the resulting α values would immediately give the selectivity relationship governing the behavior of solvolytically generated sterically similar free vinyl cations. The solvolysis of **2** and related optically active vinylic systems in solvents where $k_\alpha \geqslant k_t$ is under active study.

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References and Notes

(1) Part 26: Z. Rappoport, P. Shulman, and M. Thuval (Shoolman), *J. Am. Chem. Soc.*, **100,** 7041 (1978).

(2) (a) R. A. Sneen, J. V. Carter, and P. S. Kay, *J. Am. Chem. Soc.*, **88,** 2594 (1966); (b) D. J. Raber, J. M. Harris, R. E. Hall, and P. v. R. Schleyer, *ibid.*, **93,** 4821 (1971); (c) L. C. Bateman, M. G. Church, E. D. Hughes, C. K. Ingold, and N. A. Taher, *J. Chem. Soc.*, 979 (1940).

(3) A. Pross, *Adv. Phys. Org. Chem.*, **14,** 69 (1977); B. Giese, *Angew. Chem., Int. Ed. Engl.*, **16,** 125 (1977). However, see C. D. Johnson, *Chem. Rev.*, **75,** 755 (1975).

(4) C. D. Ritchie, *Acc. Chem. Res.*, **5,** 348 (1972); C. D. Ritchie and P. O. I. Virtanen, *J. Am. Chem. Soc.*, **94,** 4966 (1972); C. D. Ritchie in "Solute–Solvent Interactions", Vol. 2, J. F. Coetzee and C. D. Ritchie, Eds., pp 259–267, Marcel Dekker, New York, 1976.

(5) C. D. Ritchie, *J. Am. Chem. Soc.*, **93,** 7324 (1971).

(6) (a) C. K. Ingold, "Structure and Mechanism in Organic Chemistry", 2nd ed., Cornell University Press, Ithaca, N.Y., 1968, pp 483–493; (b) S. Winstein, E. Clippinger, A. H. Fainberg, R. Heck, and G. C. Robinson, *J. Am. Chem. Soc.*, **78,** 328 (1956); (c) S. Winstein, B. Appel, R. Baker, and A. Diaz, *Chem. Soc., Spec. Publ.*, **No. 19,** 109 (1965).

(7) D. J. Raber, J. M. Harris, and P. v. R. Schleyer in "Ions and Ion Pairs in Organic Reactions", Vol. II, M. Szwarc, Ed., Wiley-Interscience, New York, 1973.

(8) For review of this behavior see (a) Z. Rappoport, *Acc. Chem. Res.*, **9,** 265 (1976); (b) P. J. Stang, Z. Rappoport, M. Hanack, and L. R. Subramanian, "Vinyl Cations", Academic Press, New York, in press.

(9) Y. Apeloig, J. Greenblatt, and Z. Rappoport, unpublished results.

(10) (a) Z. Rappoport and Y. Apeloig, *J. Am. Chem. Soc.*, **96,** 6428 (1974); (b) *ibid.*, **97,** 821 (1975); (c) *ibid.*, **97,** 836 (1975).

(11) D. Scheffel, P. J. Abbott, G. J. Fitzpatrick, and M. D. Schiavelli, *J. Am. Chem. Soc.*, **99,** 3769 (1977).

(12) Satisfactory analytical and spectroscopic data were obtained for all the new compounds.

(13) Following Ingold[6a] α does not take into account the solvent concentration. When the concentration of pure TFE is taken into account, the dimensionless α is ~44 000.

(14) Potentiometric titration was used to obtain the k_t values in the absence of added Br^- or in the presence of 0.092 M Bu_4NBr. The method is not very accurate at higher concentrations of Br^-. The different UV spectra of **2** and **4** enabled a spectrophotometric followup of the **2** → **4** reaction in the presence of 0.1 M Bu_4NBr. The $k_t/k_t{}^0$ ratio is ~0.01; i.e., ≥99% of the products are derived from the free ion.

(15) Z. Rappoport and J. Kaspi, *J. Am. Chem. Soc.*, **96,** 4518 (1974).

(16) This is probably the route for loss of optical activity of **2** in AcOH, where $k_\alpha \gg k_t$ and $k_{rear}(\mathbf{6}) \gg k_t{}^0(\mathbf{2})$.

(17) The extrapolated $k_t{}^0$ value is very sensitive to the accuracy of the first kinetic points. We hope to overcome this difficulty in cooperation with Dr. G. Lodder from the University of Leiden by an independent measurement of $k_t{}^0$ by following radioactive Br^- incorporation. Until then, the similarity of $k_t{}^0$ and k_α should be regarded only as approximate.

(18) The fractions of ion-pair return 1-F are 0.63 for α-bromo-β-deuterio-*p*-methoxystyrene in AcOH,[10a] and 0.47[10b] and 0.32–0.39[10c] for 1,2-dianisyl-2-phenylvinyl bromide in AcOH and in 80% EtOH, respectively.

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On the Reported Selectivity of Olefin Bromination

Sir:

In a recent issue of the *Journal of the American Chemical Society* there appeared a report about a novel selective bromination agent consisting of bromine adsorbed on 5-Å molecular sieves.[1] This selective reagent was claimed to be capable of differentiating between a double bond located in a sterically unhindered linear side chain and one in an inaccessible position, such as one within an alicyclic ring. As evidence the authors presented two observations: (1) the selective bromination of styrene in the presence of cyclohexene, and (2) the absence of bromoacetate product when run in the presence of a small amount of acetic acid.

It is most difficult to accept the interpretation of these observations as proposed by the authors, in view of the well established fact that 5-Å molecular sieves have pore openings too small to permit entry of branched hydrocarbons.[2] Accordingly, we have observed that secondary bromides such as 2-bromobutane are *not* sorbed inside 5-Å sieves at room temperature;[3] furthermore, if bromination were occurring within the sieve, the products would be retained by the sieve. We believe the observations reported can be most satisfactorily explained on the basis of the well-known dichotomy associated with olefin halogenation in general, namely the availability of competitive ionic and free-radical pathways. In the case of olefin chlorination, Poutsma[4] clearly demonstrated this duality of mechanism and identified the characteristics of each pathway. Bromination of olefins in low polarity media is also very sensitive to acceleration by light, hydrogen halides, and water and can be greatly affected by glass or silica surfaces.[5] Under ionic conditions, cyclohexene would be expected to halogenate faster than styrene, since styrene has been reported to brominate only at approximately the same rate as terminal olefins.[6] The reverse may be expected under free-radical conditions since thiyl radicals, which are considered to have reactivities similar to bromine atoms on the basis of the established bond dissociation energies of HSR and HBr, are known to add some 60 times faster to styrene than to cyclohexene.[7]

We have observed that, under competitive conditions in CCl_4 at room temperature, cyclohexene does in fact brominate ~5 times as rapidly as styrene. However, when a 10^{-2} M Br_2 solution was added dropwise to an equal volume of a CCl_4 solution, 0.02 M in styrene and in cyclohexene, while being illuminated by a photoflood lamp, the yield of 1,2-dibromoethylbenzene greatly exceeded (>10:1) that of 1,2-dibromocyclohexane. The free-radical nature of this reaction, performed in the presence of atmospheric oxygen, was confirmed by the detection of a third product, α-bromoacetophenone, formed by oxygen trapping of the intermediate β-bromobenzyl radical. Further support for a free-radical mechanism under these bromination conditions can be found in the observation of two other products by GC-mass spectroscopy: 1-chloro-2-bromoethylbenzene[8] and a trace amount of 3-bromocyclohexene. The former was formed by chlorine atom abstraction from CCl_4 by the β-bromobenzyl radical, while the latter undoubtedly derived from allylic hydrogen atom abstraction by radicals.

In view of these observations confirming the duality of mechanisms for olefinic halogenations, we believe the unusual reactivity of styrene reported for molecular sieve supported bromine to be due to free-radical reactions proceeding slowly in homogeneous solution with the small amount of soluble bromine in equilibrium with sorbed bromine. The absence of bromoacetate addition products is consistent with a free-radical mechanism, as such products would only be formed under ionic conditions.[9] The presence of 5-Å molecular sieves serves both to reduce drastically the concentration of bromine in solution and to initiate a free-radical chain reaction, which is not unexpected in view of its reported ability to catalyze the anti-Markownikoff addition of HBr to terminal olefins.[10]

Most convincing was the additional observation that, in the competitive 5-Å-supported bromination of cyclohexene and 4,4-dimethylhexene-1, a terminal olefin capable of partially penetrating the pores of the molecular sieve like styrene, but one much less susceptible to free-radical addition, the yield of dibromocyclohexene exceeded that of dibromodimethylhexane by a factor of 10. Since a similar ratio was observed in the absence of any sieves, the ionic bromination of olefins clearly is unaffected by the addition of 5-Å molecular sieves.

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References and Notes

(1) P. A. Risbood and D. M. Ruthven, *J. Am. Chem. Soc.*, **100**, 4919 (1978).
(2) D. W. Breck et al., *J. Am. Chem. Soc.*, **78**, 5963 (1956); D. W. Breck, "Zeolite Molecular Sieves", Wiley, New York, 1974.
(3) Experiment was performed by Dr. G. T. Kerr, using gas phase gravimetric analysis.
(4) M. L. Poutsma, *J. Am. Chem. Soc.*, **87**, 2161, 2172 (1965).
(5) G. A. Olah and T. R. Hockswender, Jr., *J. Am. Chem. Soc.*, **96**, 3574 (1974).
(6) M. F. Ruasse and J. E. Dubois, *J. Am. Chem. Soc.*, **97** 1977 (1975).
(7) C. Walling and W. Helmreich, *J. Am. Chem. Soc.*, **81**, 1144 (1959).
(8) Mass spectroscopy shows peaks at *m/e* 222, 220, 218; 185, 183 (–Cl); 127, 125 (–CH_2Br).
(9) Incidentally, in our hands, in the absence of styrene, cyclohexene does in fact react with bromine sorbed on 5-Å molecular sieves.
(10) L. C. Fetterly and K. F. Koetitz, *Mol. Sieves, Pap. Conf., 1967*, 102 (1968).

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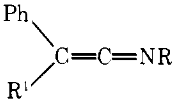
Rate-Determining Proton Transfer to Ketenimines

Sir:

We report here that *N*-alkylketenimines **1** undergo rapid reaction in aqueous solution to form the corresponding amides **5**, the slow step at all pH's being a proton transfer from acidic catalysts or the solvent. The ketenimine system can therefore even abstract a proton from such a weakly acidic species as water.

Ketenimines are heterocumulenes structurally related both to allenes and ketenes. Although chiral, they have not been resolved because of rapid nitrogen inversion.[1] They are highly reactive[2] undergoing inter alia cycloadditions and reactions with electrophilic and nucleophilic reagents and because of this they are usually generated and further reacted in situ.[3] We



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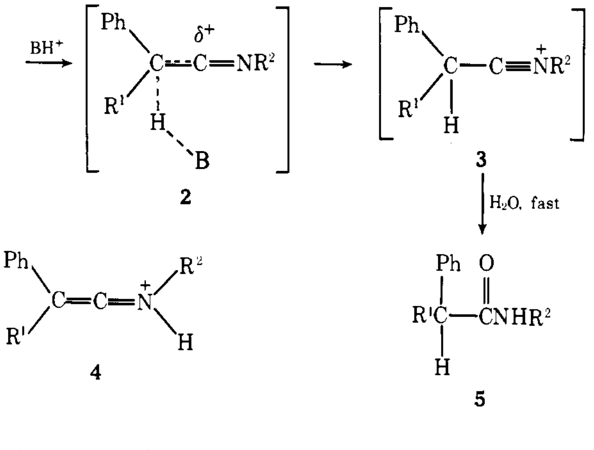

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