Mass Spectral Decompositions as a Guide to Hitherto Unrealized Reactions in Solution. Ketene Addition to the α-Methoxybenzyl Carbonium Ion

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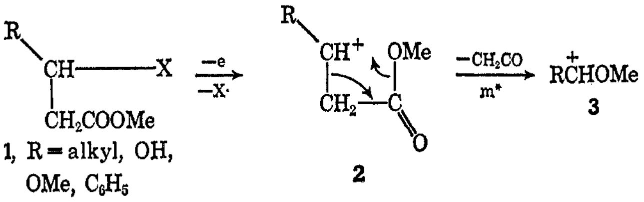
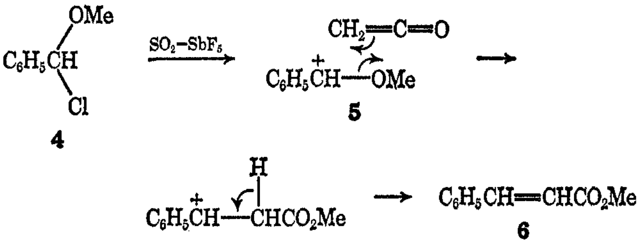
Carbonium ions of the general formula **2** may be generated upon electron impact from compounds **1** when X is lost as a radical (*e.g.*, X = Br, $COOCH_3$). It has been shown[1,2] that the lowest energy pathway for unimolecular decomposition of the carbonium ions is *via* loss of ketene in a process involving methoxy-group migration (**2** → **3**).



On the basis of the unimolecular gas-phase elimination of ketene from the carbonium ions **2**, we reasoned that the energy of activation of the back-reaction might also be relatively low, *i.e.*, that ketene addition to a α-methoxycarbonium ion, with associated methoxy-group migration, might be realized in a bimolecular reaction in solution.

The α-methoxybenzyl carbonium ion (**5**) was generated by addition of α-methoxybenzyl chloride (**4**)[3] to an SO_2–SbF_5 mixture at −70°;[4] formation of **5** was established by nmr spectroscopy. Approximately 1 equiv of ketene was passed through the solution at this temperature and the resulting mixture was quenched with ethanol. Standard isolation techniques gave a 12% yield of methyl cinnamate (**6**) and only 3% ethyl cinnamate.



The gas-phase and solution reactions involving the methoxy migration are represented as concerted only for convenience, and a stepwise process is not excluded.

This example demonstrates that unimolecular decompositions of positive ions in the mass spectrometer may on occasions serve as a guide to the reverse bimolecular reactions of carbonium ions in solution.

Experimental Section

Generation of α-Methoxybenzylcarbonium Ion.—In a typical experiment, 1.0 g of α-methoxybenzyl chloride (6.4 mmol) was added carefully to the surface of a solution of 2.0 g of SbF_5 (9.2 mmol) in 2 ml of SO_2 at −70°.[4] When the methoxybenzyl chloride had had sufficient time to cool to −70° (about 5 min), the reaction vessel was shaken to give a clear, deep red, homogeneous solution. The nmr spectrum of this solution, run at −58° on a Varian HA 100-MHz instrument, established the specific formation of the α-methoxybenzylcarbonium ion: τ 5.13 (s, 3), 1.75–2.20 (m, 5), 0.67 (s, 1).

Reaction of the Carbonium Ion with Ketene.—Approximately 1 equiv of ketene, generated by the pyrolysis of acetone, was passed through the carbonium ion solution at −70° over a period of 10 min. The product was quenched by pouring into 5 ml of ethanol at −70°; the mixture was then poured into 25 ml of water and continuously extracted with ether. The ether extract was analyzed by gas chromatography using a 4-ft LAC column at 155°, and two peaks having retention times identical with those of methyl and ethyl cinnamates were collected. The nmr and mass spectra (AEI-MS9 instrument with heated inlet) of these two fractions were identical with the corresponding spectra of the authentic esters. The yields, based on α-methoxybenzyl chloride, were 12% methyl and 3% ethyl cinnamate.

Registry No.—**5**, 23790-70-7.

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[1] I. Howe and D. H. Williams, *J. Chem. Soc., C*, 202 (1968).

[2] R. G. Cooks, J. Ronayne, and D. H. Williams, *ibid.*, 2601 (1967).

[3] F. Straus and H. Heinze, *Ann.*, **493**, 203 (1932).

[4] G. A. Olah and J. M. Bollinger, *J. Amer. Chem. Soc.*, **89**, 2993 (1967).

The Effect of Solvents with Basic Oxygen in Epoxidation with Organic Peroxy Acids

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The intramolecularly hydrogen-bonded peroxy acid molecule (or the dipolar form derived from it) has been recognized as the initial reactive species in the epoxidation reaction.[1]

Any reduction in the effective concentration of the cyclically bonded peroxy acid should thus reduce the rate of epoxidation. That epoxidation proceeds at a considerably slower rate in solvents capable of intermolecular association has already been clearly shown by Renolen and Ugelstad.[2]

Schwartz and Blumbergs[3] were the first to measure changes in the carbonyl frequency of *m*-chloroperoxybenzoic acid in methylene chloride containing acetonitrile, suggesting intermolecular association between peroxy acid and acetonitrile, but no further systematic attempts were made, to our knowledge, (1) to confirm or reject this type of association spectroscopically, or (2) to correlate the strength of the intermolecular hydrogen bonding with kinetic and activation parameters of epoxidation in these solvents. The infrared and kinetic studies to clarify this problem have been carried out and are discussed in this paper.

The lowering of the OH stretching frequencies and broadening of the corresponding OH stretching bands of *p*-nitroperoxybenzoic acid in ethyl acetate, diethyl ether, dioxane, tetrahydrofuran, and dimethylformamide, respectively, compared with intramolecularly

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[1] A. Ažman, B. Borštnik, and B. Plesničar, *J. Org. Chem.*, **34**, 971 (1969), and references cited therein.

[2] P. Renolen and J. Ugelstad, *J. Chim. Phys.*, **57**, 634 (1960).

[3] N. N. Schwartz and J. Blumbergs, *J. Org. Chem.*, **29**, 1976 (1964).

TABLE I

INFRARED DATA AND KINETIC PARAMETERS OF EPOXIDATION OF *trans*-STILBENE (4.0–4.3 × 10^{-2} *M*) WITH *p*-NITROPEROXYBENZOIC ACID (4.8–5.2 × 10^{-2} *M*) IN SOLVENTS WTH BASIC OXYGEN

Solvent	DC,[a] ε	DM,[a] μD	pK_b[b]	$\Delta\nu_{OH}$[c] (±8 cm^{-1})	$k_2 \times 10^4$, l./mol sec			E_a, kcal/mol	ΔS^*, eu, at 20°
					20°	25°	30°		
Methylene chloride	8.9	1.5	. . .	0	55.5	. . .	118	13.3	−25.4
Ethyl acetate	6.2	1.85	19.1	33	2.72	4.41	7.09	16.9	−19.1
Diethyl ether	4.2	1.25	17.6	115	0.87	1.47	1.99[d]	18.1	−17.3
Dioxane	2.2	0.40	16.9	100	1.37	. . .	3.70	17.5	−18.3
Tetrahydrofuran	7.4	1.7	16.0	149	0.76	1.29	2.14	18.3	−17.0
Dimethylformamide	36.7	3.8	14.1	165	0.32	0.56	0.93	18.8	−16.7

[a] From "Handbook of Chemistry and Physics," 48th ed, The Chemical Rubber Co., Cleveland, Ohio, 1967. [b] From J. Perrin, "Dissociation Constants of Organic Bases in Aqueous Solution," Butterworth and Co. Ltd., London, 1965. [c] The differences in frequencies between the intramolecular hydrogen-bonded OH absorption of *p*-nitroperoxybenzoic acid in methylene chloride (3285 cm^{-1}) and intermolecular hydrogen-bonded OH absorptions in solvents with basic oxygen. [d] Measured at 28°.

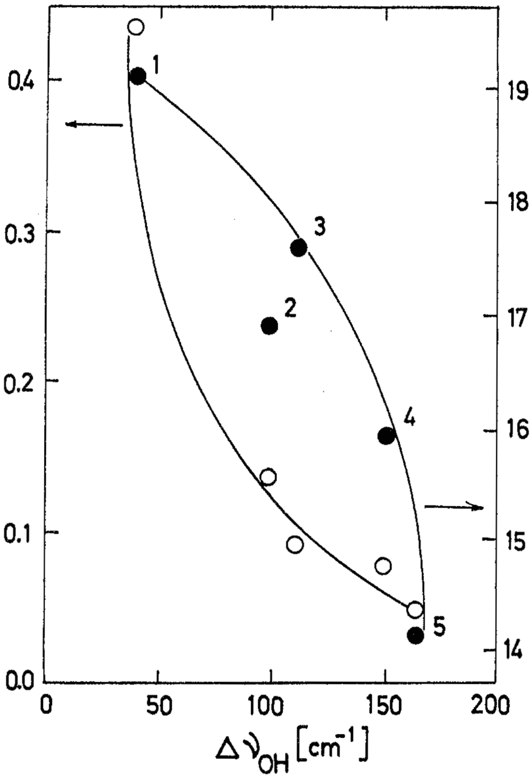
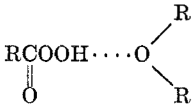


Figure 1.—Plots of logarithms of second-order rate constants of epoxidation of *trans*-stilbene with *p*-nitroperoxybenzoic acid in solvents with basic oxygen, and basicities (pK_b) of these solvents *vs.* $\Delta\nu_{OH}$, *i.e.*, the approximate strength of intermolecular hydrogen bonding between peroxy acid and a solvent: 1, ethyl acetate; 2, dioxane; 3, diethyl ether; 4, tetrahydrofuran; 5, dimethylformamide.

hydrogen-bonded OH in inert solvents, show that this peroxy acid exists in solvents with basic oxygen in the form of intermolecularly hydrogen-bonded adducts according to the following scheme.



$$\mathrm{R\overset{\overset{}{}}{C}(=O)OOH\cdots OR_2}$$

The shift of the C=O stretching frequencies of peroxy acid to higher values in these solvents could also be taken as a support for the above-mentioned conclusion[4] ($\Delta\nu_{C=O}$ = 25 cm^{-1}).

The kinetics of epoxidation of *trans*-stilbene with *p*-nitroperoxybenzoic acid in solvents under investigation was studied. The results of these measurements, along with the differences in frequencies between the intramolecular and intermolecular hydrogen-bonded OH absorptions of peroxy acid, which have been taken as a measure of an approximate strength of intermolecular association,[5] are collected in Table I.

Graphical presentation of the results in Figure 1 shows that the strength of intermolecular association between the peroxy acid molecule and a solvent increases with increasing basicity of solvents. It is also evident that the rate of epoxidation decreases in solvents which are capable of forming stronger intermolecular hydrogen bonds. The energies of activation of epoxidation are correspondingly higher in solvents which are more basic. There is a discrepancy between the expected and observed values only in the case of the solvent pair dioxane–diethyl ether. The activation energy of epoxidation, as well as $\Delta\nu_{OH}$, are higher in diethyl ether than in dioxane. It seems that diethyl ether behaves as more basic than dioxane in our system. Similar observations were made also by other workers.[6,7] An additional increase of the activation energy of epoxidation in diethyl ether in comparison with dioxane as a solvent, not expected solely on the basis of stronger intermolecular hydrogen bonding between peroxy acid and a solvent, could probably be attributed to the steric retardation in approaching the olefin molecule to the reactive center in the peroxy acid–solvent complex by methyl groups of diethyl ether.

The fact that the entropy of activation increases with increasing strength of intermolecular hydrogen bonding yields some further insight into the degree of orientation of the reactive species, *i.e.*, the greatest orientation of the peroxy acid–solvent complex in the case of solvents which form the strongest intermolecular hydrogen bonds with peroxy acid.

It is reasonable to assume on the basis of the abovementioned results that the strength of the intermolecular association between peroxy acids and solvents with basic oxygen is one of the major factors influencing the kinetics of epoxidation in these solvents, although polarizabilities and steric requirements of solvents may also influence the rate of epoxidation in those cases where the differences in basicity of solvent pairs are small.

(4) G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman and Co., San Francisco, Calif., 1960.

(5) M. Tichy, *Advan. Org. Chem.*, **5**, 115 (1965).

(6) T. Cuvigny and H. Normant, *Bull. Soc. Chim. Fr.*, 2000 (1964).

(7) H. Normant, *Angew. Chem.*, **79**, 1029 (1967).

Experimental Section

p-Nitroperoxybenzoic acid was prepared and purified according to the procedure of Silbert, *et al.*[8] All the solvents used were Reagent grade commercial products and were dried and distilled before use. The purity of each was confirmed by vapor phase chromatography. *trans*-Stilbene, scintillation grade, was obtained from Fluka and used without further purification.

The infrared spectra were recorded at 20° on a Perkin-Elmer Model 521 infrared spectrophotometer using 0.05–0.10 mm cells (NaCl). Methylene chloride solutions of equimolar amounts of peroxy acid and a compound with basic oxygen were employed.

The kinetics of epoxidation was followed iodometrically according to Lynch and Pausacker.[9] Reactions were performed in 50-ml volumetric flasks. Samples (5 ml) were quenched in 2-*N* sulfuric acid cooled and degassed with small pinches of Dry Ice, an excess of potassium iodide was added (1 ml of 15% solution), and the liberated iodine was titrated with 0.05 *N* sodium thiosulfate without starch indicator. When ethyl acetate or diethyl ether were used as solvents, carbon tetrachloride was necessary to add to the titration mixture in order to obtain satisfactory end-points. Observed titres were corrected for the decomposition of peroxy acid in the corresponding solvent. Second-order rate constants were obtained from a linear least-squares program. Calculation of activation energies and entropies was performed by the usual method.[10] Errors (standard deviations) in second-order rate constants are ±2%, those in E_a are *ca.* ±0.5 kcal/mol, and those in $\Delta S^{\ddagger}$ are ±1.5 eu.

Registry No.—*trans*-Stilbene, 103-30-0; *p*-nitroperoxybenzoic acid, 943-39-5.

Acknowledgment.—The authors wish to thank Professor D. Hadži for his interest and encouragement. The financial support of this research by the Boris Kidrič Fund is also gratefully acknowledged.

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[8] L. S. Silbert, E. Siegel, and D. Swern, *J. Org. Chem.*, **27**, 1136 (1962).

[9] B. M. Lynch and K. H. Pausacker, *J. Chem. Soc.*, 1525 (1955).

[10] J. F. Bunnett, "Investigation of Rates and Mechanisms of Reaction," Part I, S. L. Friess, E. S. Lewis, and A. Weissberger, Ed., 2nd ed, Interscience Publishers, Inc., New York, N. Y., 1961.

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pK_a Values of 4-Substituted 4′-Aminobenzanilides and 4′-Hydroxybenzanilides. A Search for Transmission of Electronic Effects through an Amide Linkage

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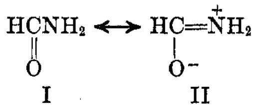
The planarity and restricted rotation of amide groups have been attributed to a dipolar resonance contributor II. Pauling[1] has estimated that I and

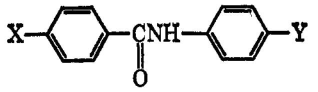


$$\mathrm{H}\underset{\underset{\displaystyle\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{NH_2} \longleftrightarrow \mathrm{H}\underset{\underset{\displaystyle\mathrm{O^-}}{|}}{\mathrm{C}}{=}\overset{+}{\mathrm{N}}\mathrm{H_2}$$

I II

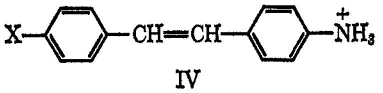
II contribute 60 and 40%, respectively, corresponding to 40% double-bond character for the C–N bond. One might expect, therefore, that two aromatic rings joined by an amide group would be conjugatively linked *via* the partial double bond. We show below that, on the contrary, there is no conjugative transmission in the ground states of compounds III.[2]

The degree of electronic interaction between the aromatic rings of IIIa and IIIb was estimated from

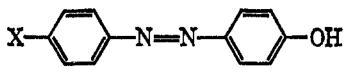


IIIa, Y = $\overset{+}{\mathrm{N}}\mathrm{H_3}$
b, Y = OH

the pK_a values presented in Table I. Since the pK_a values of the corresponding stilbenes (IV) and azobenzenes (V) are known,[3–5] it is possible to compare the amide group with the ethylene and azo functionalities.



IV



V

Table I

pK_a Values of 4-Substituted 4′-Aminobenzanilides and 4′-Hydroxybenzanilides (IIIa and IIIb)[a]

Y	X	pK_a
$\overset{+}{\mathrm{N}}\mathrm{H_3}$	OCH_3	4.62
$\overset{+}{\mathrm{N}}\mathrm{H_3}$	CH_3	4.52
$\overset{+}{\mathrm{N}}\mathrm{H_3}$	H	4.55
$\overset{+}{\mathrm{N}}\mathrm{H_3}$	Cl	4.54
$\overset{+}{\mathrm{N}}\mathrm{H_3}$	NO_2	4.48
OH	OCH_3	9.55
OH	CH_3	9.54
OH	H	9.54
OH	Cl	9.50
OH	NO_2	9.50

[a] Determined spectrophotometrically in 1.6% acetonitrile–water at 25.0°.

The Hammett ρ value for IIIa, calculated from the data in Table I, was found to be 0.09 ± 0.04 in 1.6% acetonitrile–water. This is considerably less than the ρ value for ionization of IV (0.422[3] and 0.684[4] in ethanol–water). The small ρ for IIIa cannot be attributed to an unusually small double-bond character of the amide C–N bond because the benzanilides show normal amide carbonyl bands in the infrared and because the presence of two phenyl rings should, if anything, enhance the contribution from the dipolar structure II. However, the possibility existed that resonance between the phenyl rings was unimportant in the conjugate base of IIIa because this would lead to a tetrapolar contributor. For this reason we determined the pK_a values of IIIb, a system

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[1] L. Pauling, "Symposium on Protein Structure," A. Newberger, Ed., John Wiley & Sons, Inc., New York, N. Y., 1958, p 17.

[2] Conjugation in the excited state of benzanilides has been demonstrated by V. A. Izmail'skii and A. V. Malygina, *Zh. Obshch. Khim.*, **29**, 3935 (1959).

[3] H. Veschambre and A. Kergomard, *Bull. Soc. Chim. Fr.*, 336 (1966).

[4] M. Syz and H. Zollinger, *Helv. Chim. Acta*, **48**, 517 (1965).

[5] S. Yeh and H. H. Jaffé, *J. Amer. Chem. Soc.*, **81**, 3287 (1959).