hydrogenation of benzene recently described by Muetterties and Hirsekorn[21] we do call attention to the similarity between our free-radical mechanism and that which has been advanced for the $HCo(CN)_5{}^{3-}$-catalyzed hydrogenation of conjugated olefins.[22] In this connection, we suggest that the hydrogenation of alkenes which typically accompanies hydroformylation, and which is especially pronounced for α,β-unsaturated compounds and at high temperatures, may also derive from this type of free-radical mechanism.[23]

We are continuing this investigation with a view to testing the above interpretations and predictions, and elucidating possible mechanisms of hydrogenation of coal-related substances.

References and Notes

(1) Supported by the Office of Molecular Studies, U.S. Energy Research and Development Administration.

(2) I. Wender, R. Levine, and M. Orchin, *J. Am. Chem. Soc.*, **72**, 4375 (1950).

(3) I. Wender, H. Greenfield, and M. Orchin, *J. Am. Chem. Soc.*, **73**, 2656 (1951).

(4) S. Friedman, S. Metlin, A. Svedi, and I. Wender, *J. Org. Chem.*, **24**, 1287 (1959).

(5) P. D. Taylor and M. Orchin, *J. Org. Chem.*, **37**, 3913 (1972).

(6) For recent reviews see (a) B. R. James, "Homogeneous Hydrogenation", Wiley, New York, N.Y., 1973, Chapter X; (b) M. Orchin and W. Rupilius, *Catal. Rev.*, **6**, 85 (1972); M. Orchin, *Adv. Catal.*, **16**, 1 (1966).

(7) A somewhat different free-radical mechanism for $HCo(CO)_4$ catalyzed hydrogenation of aldehydes under hydroformylation conditions was first mentioned in ref 2. This mechanism invokes H-atom intermediates, formed by a path which is now known to be energetically very unfavorable;[19] this reduction was later shown not to be free-radical in nature.[20] In contrast, all of the steps of our mechanistic scheme, eq 1, are energetically accessible for the substrates under consideration.

(8) T. A. Weil, S. Friedman, and I. Wender, *J. Org. Chem.*, **39**, 48 (1974).

(9) 9,10-Cis-addition of $HCo(CO)_4$, hydrogen abstraction by the bound $Co(CO)_4$ from the neighboring methyl group, and anti-Markovnikov addition of $HCo(CO)_4$ from either side to the resulting methylene compound.

(10) (a) M. Levy and M. Szwarc, *J. Chem. Phys.*, **22**, 1621 (1954); (b) M. Szwarc, *J. Phys. Chem.*, **61**, 40 (1957); (c) M. Szwarc and J. H. Binks, *Chem. Soc., Spec. Publ.*, **No. 12**, (1959); (d) C. A. Coulson, *J. Chem. Soc.*, 1435 (1955).

(11) Rate constants[12] were calculated from $k_i = -\ln f_i/tC$, where f_i = fraction of substrate i unconverted, t = time at temperature, C = concentration of active catalyst. Reactivities, $R_i = k_i/N_i$, where N_i is the number of equivalent positions of greatest reactivity.[13] The time, t, was assumed to be the same in each experiment (5 hr for the example described).

(12) The rate of hydrogenation has been shown to be first order in substrate concentration and proportional to the active catalyst concentration. H. M. Feder, R. D. Wolson, L. E. Ross, and J. Rathke, to be submitted for publication.

(13) (a) C. A. Coulson and S. Streitwieser, Jr., "A Dictionary of Pi-Electron Calculations", W. H. Freeman, San Francisco, Calif., 1965; (b) A. Streitwieser, Jr., and J. I. Bauman, "Supplemental Tables of Molecular Orbital Calculations", Pergamon Press, Oxford, 1965. The localization energies are those for positions of highest free-valence; N_i is the number of such equivalent, most reactive, positions.

(14) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists", Wiley, New York, N.Y., 1961, Chapter 13.

(15) The position of the nonalternant hydrocarbon fluoranthene on this plot also implies that the transition state has little or no polarity because the localization energies of the corresponding fluoranthene anion and cation are widely different from that of the neutral radical.

(16) Both 9,10-dihydro- and 1,2,3,4-tetrahydrophenanthrene are products of phenanthrene hydrogenation in ~7:1 ratio.[2,5] Unfortunately, quantitative prediction of this ratio is hindered by the closeness of the localization energies corresponding to the alternative modes of attack, and the possibility of steric effects.[14]

(17) Under sufficiently high CO and H_2 pressures to maintain the catalyst predominantly in the $HCo(CO)_4$ form.[18,19]

(18) (a) Y. E. Bronshtein, V. Yu Gankin, D. P. Krinkin, and D. M. Rudkovskii, *Zh. Fiz. Khim.*, **40**, 2493 (1966), also *Russ. J. Phys. Chem.*, **40**, 802 (1966); (b) Yu E. Bronshtein, V. Yu Gankin, N. I. Kalashnikova, D. P. Krinkin, D. M. Rudkovskii, and M. N. Sorokin, *Russ. J. Phys. Chem.*, **40**, 1337 (1966).

(19) (a) F. Ungvary and L. Marko, *J. Organomet. Chem.*, **20**, 205 (1969); F. Ungvary, *ibid.*, **36**, 363 (1972).

(20) C. L. Aldridge and H. B. Jonassen, *J. Am. Chem. Soc.*, **85**, 886 (1963).

(21) (a) E. L. Muetterties and F. J. Hirsekorn, *J. Am. Chem. Soc.*, **96**, 4063 (1974); (b) F. J. Hirsekorn, M. C. Rakowski, and E. L. Muetterties, *ibid.*, **97**, 237 (1975).

(22) (a) J. Kwiatek, *Catal. Rev.*, **1**, 37 (1968), and references therein; (b) J. Halpern and L. Y. Wong, *J. Am. Chem. Soc.*, **90**, 6665 (1968).

(23) This view is supported by the observation[24] that hydroformylation of α-ethylstyrene with an optically active cobalt catalyst, containing a chiral Schiff's base ligand, yields some optically active aldehyde whereas the accompanying hydrogenation product, 2-phenylbutane, is completely inactive.

(24) P. Pino, G. Consiglio, C. Botteghi, and C. Salomon, *Adv. Chem. Ser.*, **No. 132**, 295 (1974).

Harold M. Feder*
Chemical Engineering Division, Argonne National Laboratory
Argonne, Illinois 60439

Jack Halpern*
Department of Chemistry, The University of Chicago
Chicago, Illinois 60637

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Bifunctional Catalysis of the Enolization of Acetone[1]

Sir:

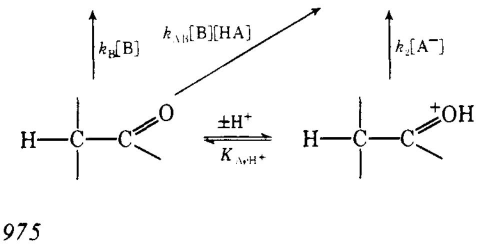
We wish to report that the third-order term for acid-base catalysis of acetone enolization exhibits a Bronsted β_{AB} value of 0.15, a solvent isotope effect of $k_{H_2O}/k_{D_2O} = 2.0$, and a C-H isotope effect of $k_H/k_D = 5.8$. We conclude that this reaction represents true bifunctional catalysis with partial proton abstraction by acetate ion and a significant movement of the proton of acetic acid toward the carbonyl oxygen atom in the transition state.

The interpretation of the third-order term, $k_{AB}[HA][B]$, in the rate law for acetone enolization (eq 1)

$$k_{obsd} = k[H_2O] + k_{H^+}[H_3O^+] + k_{HO^-}[HO^-] + k_A[HA] + k_B[B] + k_{AB}[HA][B] \quad (1)$$

has been the subject of much controversy and has played an important role in the development of ideas on the mechanism of acid-base catalysis in solution and at the active sites of enzymes.[2] In particular, attempts have been made, and criticized, to interpret *all* of the rate terms as bifunctional, third-order acid-base catalysis in which water may cooperate in the rate-determining step as an acid-base species.[2,3] A reexamination of this problem appeared warranted because the mechanism for the k_A and k_B terms is now known. The k_A term has been shown to represent catalysis by the proton of the removal of a proton by acetate ion (k_2/K_{AcH^+}, Scheme I),[4,5] most directly by the demonstration that the rate of the reverse, ketonization reaction of RCH=CR′OH is entirely accounted for by the rate of protonation of the corresponding enol ether, $RCH{=}CR'OCH_3$, in which proton removal from $-OCH_3$ in the transition state is impossible.[5] Thus, the proton is fully transferred to the carbonyl oxygen atom in the transition state (i.e., a = 1.0). The k_B term (general base catalysis of C-H proton removal) can only involve stabilization of the transition state by hydrogen bonding of the carbonyl oxygen atom to water because there is no thermodynamic advantage to the transfer of a proton from water to the enolate ion (p$K \approx 11$); a for this reaction is, therefore, ca. 0-0.2.[6] One of us (W.P.J.) suggested that the third-order term represents simply a modification of the k_B term, in which acetic acid instead of water is hydrogen bonded to the transition state.[6] Since the value of a_A for hydrogen bonding is

Scheme I



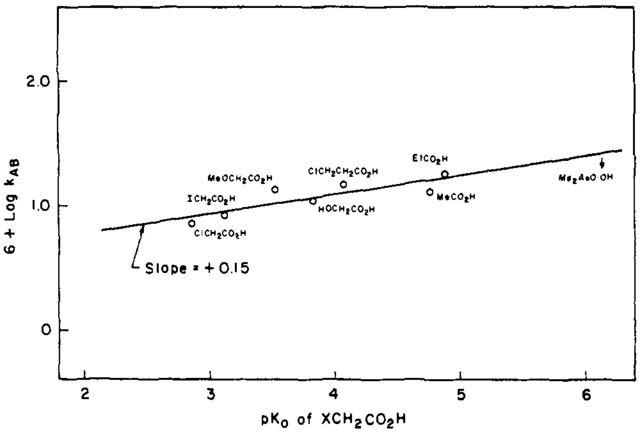


Figure 1. Bronsted plot of the third-order rate constants for catalysis of acetone enolization by acid-base pairs at 25°, ionic strength 2.0 (KNO_3). Initial rates were measured by iodination with buffer concentrations of 0-2 *M* as described previously;[6] control experiments showed no major specific salt or solvent effects.

close to 0.2,[7] the same as is found for many carbonyl addition reactions,[8] and the value of β_B is 0.88,[2] it was predicted that the value of β_{AB} for the third-order term would be 0.88-0.2 or approximately 0.68.

In fact, the magnitude of the third-order term is almost independent of the p*K* of the acid-base pair used, with a value of $\beta_{AB} = 0.15$ (Figure 1). The third-order term could be detected for all carboxylic acids of p$K \geq 2.8$ but not for cacodylic acid, for which an upper limit is shown in the figure. The small Bronsted slope means that when the p*K* of the acid-base pair is increased the increase in the effectiveness of the catalyzing base is largely cancelled by a decrease in the effectiveness of the catalyzing acid. The dependence on the base strength of B must lie between $\beta_B = 0.88$ (no protonation of the carbonyl oxygen) and $\beta_B = 0.45$[9] (complete protonation of the carbonyl oxygen). The dependence on the strength of the catalyzing acid must therefore be relatively large ($\alpha_A \sim 0.5$) for the third-order term to account for the observed β_{AB} of 0.15.[10]

The C-H isotope effect for the third-order term was determined from the rates of enolization of CH_3COCH_3 and CD_3COCD_3 with AcOH and AcO^- as catalysts. The observed rate constant ratio of 5.8 gives a normal primary isotope effect (uncorrected for secondary effects of adjacent C-H groups) similar to values previously reported for acid and base catalyzed enolization[4a,11] and indicates considerable C-H (or C-D) bond cleavage in the transition state. The solvent deuterium isotope effect for the third-order term was found to be $k_{H_2O}/k_{D_2O} = 2.0$ for both CH_3COCH_3 and CD_3COCD_3. In contrast, the solvent deuterium isotope effect is only 1.0-1.25 for k_B and 1.1-1.5 for k_A;[4b,11,12] the latter value corresponds to a value of $k_{H_2O}/k_{D_2O} = 0.9$-1.2 for proton abstraction by acetate from protonated acetone, after correction for isotope effects on the dissociation constants of HOAc and $CH_3COHCH_3^+$.[13] The larger value for the k_{AB} term shows that there is a significant loss of H-O zero-point energy in the transition state.

The catalytic constants for trimethylamine *N*-oxide (pK_a = 4.95, $k_A = 20 \times 10^{-6}\ M^{-1}\ \mathrm{min}^{-1}$, $k_B = 50 \times 10^{-6}\ M^{-1}\ \mathrm{min}^{-1}$, $k_{AB} = 140 \times 10^{-6}\ M^{-2}\ \mathrm{min}^{-1}$) are significantly larger, especially the third-order term, than those for acetic acid (pK_a = 4.68, $k_A = 4.8 \times 10^{-6}\ M^{-1}\ \mathrm{min}^{-1}$, $k_B = 12.5 \times 10^{-6}\ M^{-1}\ \mathrm{min}^{-1}$, $k_{AB} = 12.6 \times 10^{-6}\ M^{-2}\ \mathrm{min}^{-1}$). This shows that special structural features of carboxylic acids or their conjugate bases are not required for any of these catalytic terms.

These results, particularly the value of $\alpha_A = 0.5$ and the solvent isotope effect $k_{H_2O}/k_{D_2O} = 2.0$ for the third-order term, establish that the mechanism of bifunctional catalysis of the enolization of acetone is different from the mechanism of either the second-order base-catalyzed or acid-catalyzed reactions, with a significant movement of the proton from the catalyzing acid toward the carbonyl oxygen atom in the transition state. Although we do not yet wish to exclude other mechanisms, the data appear to be consistent with the hypothesis that the two proton transfers in the third-order reaction are truly concerted.

References and Notes

(1) Publication No. 1053 from the Graduate Department of Biochemistry, Brandeis University, Waltham, Mass. 02154. This work was supported by grants from the National Science Foundation (BM571-01501 AO3) and the National Institute of General Medical Sciences of the National Institutes of Health (GM20888). A.F.H. was on leave from the Department of Chemistry, University College, Cork, Ireland.

(2) H. M. Dawson and E. Spivey, *J. Chem. Soc.*, 2180 (1930); R. P. Bell, "The Proton in Chemistry", 2nd ed, Cornell University Press, Ithaca, N.Y., 1973, Chapter 8.

(3) K. J. Pederson, *J. Phys. Chem.*, **38,** 590 (1934); C. G. Swain, *J. Am. Chem. Soc.*, **72,** 4578 (1950); R. P. Bell and P. Jones, *J. Chem. Soc.*, 88 (1953).

(4) (a) C. G. Swain, E. C. Stivers, J. F. Renwer, Jr., and L. J. Schaad, *J. Am. Chem. Soc.*, **80,** 5885 (1958); (b) C. G. Swain, A. J. DiMilo, and J. P. Cordner, *ibid.*, **80,** 5983 (1958); (c) C. G. Swain and A. S. Rosenberg, *ibid.*, **83,** 2154 (1961); (d) J. Toullec and J. E. Dubois, *ibid.*, **96,** 3524 (1974).

(5) G. E. Lienhard and T. C. Wang, *J. Am. Chem. Soc.*, **91,** 1146 (1969).

(6) E. Hand and W. P. Jencks, *J. Am. Chem. Soc.*, **97,** 6221 (1975).

(7) R. W. Taft, D. Gurka, L. Joris, P. v. R. Schleyer, and J. W. Rakshys, *J. Am. Chem. Soc.*, **91,** 4801 (1969).

(8) J. M. Sayer and W. P. Jencks, *J. Am. Chem. Soc.*, **91,** 6353 (1969), and references therein.

(9) R. P. Bell and O. M. Lidwell, Proc. R. Soc. London, *Part A*, **176,** 88 (1940). The value of $\alpha = 0.55$ for the k_A term is equivalent to $\beta = 1 - \alpha = 0.45$ for k_2/K_{AcH^+} (C. G. Swain, A. J. DiMilo, and J. P. Cordner, *J. Am. Chem. Soc.*, **80,** 5983 (1958)).

(10) The unique set of values that satisfies the equations $\beta_{AB} = 0.15$ and $\beta_{AB} = \beta_B - \alpha_A$ is $\beta_B = 0.66$ and $\alpha_A = 0.51$, assuming that β_B is a linear function of α_A from $\beta_B = 0.88$ for $\alpha_A = 0$ to $\beta_B = 0.45$ for $\alpha_A = 1.0$.

(11) O. Reitz and J. Kopp, *Z. Phys. Chem., Abt. A*, **184,** 429 (1939).

(12) P. T. MacTigue and J. M. Sune, *Aust. J. Chem.*, **20,** 905 (1967); F. A. Long and D. Watson, *J. Chem. Soc.*, 2021 (1958); O. Reitz, *Z. Phys. Chem., Abt. A*, **179,** 119 (1936); D. B. Dahlberg and F. A. Long, *J. Am. Chem. Soc.*, **95,** 3825 (1973).

(13) The solvent effect for the dissociation constant of acetic acid is 3.3 (D. M. Laughton and R. E. Robertson, "Solute-Solvent Interactions", J. G. Coetzee and C. D. Ritchie, Ed., Marcel Dekker, New York, N.Y., 1969, p 407) and a value of 2.7 for the dissociation constant of protonated acetone has been estimated by J. Toullec and J. E. DuBois (*J. Am. Chem. Soc.*, **96,** 3524 (1974)).

A. F. Hegarty, W. P. Jencks*
Graduate Department of Biochemistry, Brandeis University
Waltham, Massachusetts 02154

Received August 4, 1975

Intramolecular Charge Transfer Quenching in Excited β-Vinyl Phenyl Ketones[1]

Sir:

There is now general agreement that, when triplet energy transfer is endothermic, olefins interact with excited ketones by a charge transfer process which probably yields an exciplex intermediate.[2,3] The complexes collapse to oxetane products in variable and often low quantum yields. Synthetically interesting bicyclic oxetanes are known to be formed upon irradiation of various unsaturated ketones.[4-7] Such intramolecular excited state interactions are gaining increased attention,[5,8] but there is very little quantitative information available which indicates how rapidly, in bifunctional compounds, intramolecular interactions compete with normal decay reactions of individual chromophores. We have now obtained this information for two γ,δ-unsaturated phenyl ketones by (1) monitoring the cis-trans photoisomerization of 1-phenyl-4-hexene-1-one, **1**, and (2) monitoring the type II photoelimination of 1-phenyl-2-ethyl-4-pentene-1-one, **2**. In both cases the β-vinyl group quenches ≥99% of