Previous reports on the electronic structure of protonated ketones vary in their terminology, but the spectroscopic results are by now generally consistent with each other and with the conclusions presented by us. In a series of papers, Olah and coworkers[13] report nmr studies of protonated alicyclic and aliphatic ketones and protonated aldehydes. On the basis of CO$^+$H proton signals at very low fields, they originally considered the protonated ketones studied by them to be represented best as oxonium ions ($>$C$=$O$^+$H), the alternative hydroxycarbonium ion valence bond form ($>$C$^+$–OH) being of lesser importance in the resonance hybrid. However, their more recent ^{13}C work indicates variation of charge delocalization as a function of the carbonyl base. Deno[14] considers the hydroxycarbonium ion form of protonated ketones to be a significant contributor to the resonance hybrid, based on comparison of the uv spectra for a series of protonated unsaturated and aromatic ketones with their corresponding carbonium ions. Brouwer[15] has used the terms "hydroxycarbonium ion" and "protonated ketone" interchangeably in his recent nmr study of protonated dialkyl ketones. Based on the observation that δ CO$^+$H in $R_1R_2CO^+H$ varies by 5 ppm (11–16 ppm), Levy and Winstein[16] adopted the view that charge distribution may be varied from largely oxonium ion to almost completely hydroxycarbonium ion[17,19] by changing the substituents on the carbonyl group. This viewpoint is supported by the observation that the energy barrier to interconversion about a protonated or alkylated carbonyl bond is quite sensitive to the electron-donating ability of the rest of the molecule.[21,22] A comparison of δ CO$^+$H values with $\Delta\bar{H}_{a,b}$ for benzophenone (12.23 ppm,[20] -16.9 kcal/mol), 4-chlorobenzophenone (12.50 ppm,[18] -15.6 kcal/mol), and 4-bromobenzophenone (12.60 ppm,[18] -15.1 kcal/mol) shows a trend of decreasing chemical shift with increasing exothermicity. Such a correlation might be anticipated in light of Birchall and Gillespie's finding[23] that δ CO$^+$H for *para*-substituted acetophenones gives linear correlations with σ^+ and pK_{BH^+}. It has been recognized,[4] however, that there is no single correlation between δ CO$^+$H and $\Delta\bar{H}_{a,b}$ for all types of ketones (aromatic, aliphatic, etc.).

The work described here provides thermodynamic information for a case where structural conditions favoring resonance delocalization of charge in the protonated species have been optimized. We have found a close similarity of the response to substituent change for the two protonation reactions as manifested by the order and magnitude of $\Delta\bar{H}_{a,b}$. This suggests strongly a similar mode of charge delocalization in both series of ions.

Edward M. Arnett, John V. Carter, Roderic P. Quirk
Department of Chemistry, University of Pittsburgh
and Mellon Institute of Carnegie-Mellon University
Pittsburgh, Pennsylvania 15213

Received November 12, 1969

---

[13] (a) C. U. Pittman, Jr., and G. A. Olah, *J. Amer. Chem. Soc.*, **87**, 5123 (1965); (b) G. A. Olah, D. H. O'Brien, and M. Calin, *ibid.*, **89**, 3582 (1967); (c) G. A. Olah, M. Calin, and D. H. O'Brien, *ibid.*, **89**, 3586 (1967); (d) G. A. Olah and M. Calin, *ibid.*, **90**, 938 (1968); (e) G. A. Olah and A. M. White, *ibid.*, **91**, 5801 (1969).

[14] N. C. Deno, *Progr. Phys. Org. Chem.*, **2**, 182 (1964).

[15] D. M. Brouwer, *Rec. Trav. Chim. Pays-Bas*, **86**, 879 (1967).

[16] G. C. Levy and S. Winstein, Abstracts of Papers, 158th National Meeting of the American Chemical Society, New York, N. Y., 1969, ORGN 111.

[17] Sekuur and Kranenburg[18] have reported δ CO$^+$H values for several substituted benzophenones in SbF_5–HSO_3F at low temperature. They range from 12.47 (4,4'-dibromo) to 13.70 (2,4,5-trimethyl) ppm downfield from TMS, intermediate between the extremes noted by Levy and Winstein.

[18] Th. J. Sekuur and P. Kranenburg, *Tetrahedron Lett.*, **39**, 4793 (1966).

[19] Hogeveen [H. Hogeveen, *Rec. Trav. Chim. Pays-Bas.*, **86**, 696 (1967)] reports δ CO$^+$H of 15.13 ppm for acetone in HF–BF_3 at $-80°$; this resonance is reported to occur at 14.24 ppm in a 9:7:2 molar SO_2–FSO_3H–SbF_5 mixture at $-59°$.[20] Thus, medium effects on these chemical shifts can be substantial.

[20] M. Brookhart, G. C. Levy, and S. Winstein, *J. Amer. Chem. Soc.*, **90**, 1735 (1968).

[21] M. Brookhart, Ph.D. Thesis, U.C.L.A., 1968.

[22] Taft [B. G. Ramsey and R. W. Taft, *J. Amer. Chem. Soc.*, **88**, 3058 (1966)] reports a free energy barrier to interconversions in the dimethoxymethyl cation of 15 kcal/mol and estimates a π-bond order of 0.2–0.3 for the C$^+$–O bonds in this ion.

[23] T. Birchall and R. J. Gillespie, *Can. J. Chem.*, **43**, 1045 (1965).

Photolysis of Benzaldehyde in Solution Studied by Nuclear Magnetic Resonance Spectroscopy

Sir:

We wish to report evidence which indicates that the photolysis of benzaldehyde in solution leads to a radical pair as one of the reaction intermediates. This evidence was obtained by measuring the nmr spectrum of ground-state benzaldehyde and its products during optical irradiation. This technique has been employed previously to study anthraquinone in its excited triplet state,[1] and the details will not be repeated here. In essence, this technique enables one to detect short-lived paramagnetic intermediates (species with unpaired electrons) which, although they exist in very low concentrations, can be observed because the unpaired electrons strongly polarize the nuclear spins. This polarization is retained when the intermediate is converted to a stable diamagnetic state such as the ground state of the starting material or products. Because the nuclear spin states have populations different from those expected for a Boltzmann distribution,[2] the nmr spectrum contains enhanced absorption and emission lines.[1,3]

For benzaldehyde, the resulting spectra are given in Figure 1. Figure 1a gives the spectrum of benzaldehyde in perdeuteriobenzene at 25° before optical irradiation. The field increases from left to right, and this spectrum is a time average of 12 scans. Figure 1b, which is a time average of two scans, illustrates the spectrum of the same solution obtained during irradiation with 2000–4000-Å light. Since Figure 1b represents fewer scans than Figure 1a, it is clear that both the aldehyde and ring proton nmr lines are enhanced during optical irradiation and that the enhancement is larger for the aldehyde proton. This enhancement appears as soon as the irradiation is started. In addition one line appears at higher field as an emission line. When optical irradiation is stopped, all of the lines relax in less than 10 sec to absorption lines having substantially lower intensities than the lines observed during irradiation.

---

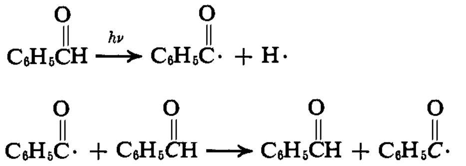
[1] M. Cocivera, *J. Amer. Chem. Soc.*, **90**, 3261 (1968).

[2] A. Abragam, "The Principles of Nuclear Magnetism," Oxford University Press, London, 1961.

[3] Other workers have been able to study thermally generated free-radical intermediates in a similar manner by measuring the nmr of the stable products resulting from these free radicals. For a brief review, see H. Fischer and J. Bargon, *Accounts Chem. Res.*, **2**, 110 (1969).

The spectrum obtained during optical irradiation can be explained by the radical-pair formation mentioned above. In presenting the arguments in favor of this process, the initial discussion will be restricted to the results for the aldehyde proton resonance. Later in the communication, it will be clear that the rest of the spectrum is consistent with the proposed mechanism.

As illustrated in Figure 1a and b, the nmr line of the aldehyde proton is enhanced during irradiation. Three mechanisms are consistent with this result. When benzaldehyde is excited, it returns to its ground state (1) *via* its triplet state, (2) according to eq 1, and (3) *via* reaction with a ground-state molecule to form a radical pair.



$$C_6H_5\overset{O}{\overset{\|}{C}}H \xrightarrow{h\nu} C_6H_5\overset{O}{\overset{\|}{C}}\cdot + H\cdot$$

$$C_6H_5\overset{O}{\overset{\|}{C}}\cdot + C_6H_5\overset{O}{\overset{\|}{C}}H \longrightarrow C_6H_5\overset{O}{\overset{\|}{C}}H + C_6H_5\overset{O}{\overset{\|}{C}}\cdot \qquad (1)$$

For the following reasons, the radical-pair mechanism seems to be the most likely explanation. Polarization while the molecule is in the triplet state seems unlikely because the polarization occurs to about the same extent when the solutions are degassed or air saturated. In the study of anthraquinone for which the triplet mechanism is believed to occur,[1] it has been found[4] that no non-Boltzmann polarization occurs when the solution is air saturated. Probably oxygen in the solution shortens the lifetime of triplet anthraquinone to prevent nuclear polarization. We feel that oxygen would have a similar effect on the polarization of the aldehyde proton if its aldehyde triplet state were responsible. Consequently it seems unlikely that the triplet-state mechanism can account for the enhancement of the aldehyde proton line.

This conclusion is based on the assumption that the rate of oxygen quenching is the same for benzaldehyde and anthraquinone. The following argument supports this assumption. Oxygen quenching is a triplet energy-transfer process involving anthraquinone or benzaldehyde as the donor and oxygen as the acceptor. When the triplet-state energy of the donor is greater than the triplet-state energy of the acceptor by 3 kcal or more, the energy-transfer rate is diffusion controlled.[5,6] The triplet-state energies for benzaldehyde and anthraquinone are 71 and 63 kcal, respectively.[7] The $^3\Sigma_g^- \rightarrow {}^1\Sigma_g^+$ transition for oxygen requires 37.5 kcal.[7] (This is the transition which is probably involved in the energy-transfer process.) Consequently a diffusion-controlled quenching rate seems likely for benzaldehyde and anthraquinone.

The results for the photolysis of benzaldehyde dissolved in carbon tetrachloride rule out the mechanism given by eq 1. The nmr spectrum of benzaldehyde in CCl_4 before and during irradiation are shown in Figure 1c and d, respectively.[8] Both are a time average of three passes. Clearly, the aldehyde proton resonance, which occurs at lowest field, is enhanced. If the mechanism given by eq 1 were occurring, no enhancement would be expected in CCl_4 because CCl_4 is a good chain-transfer agent for radicals.[9] Thus, eq 1 seems unlikely.

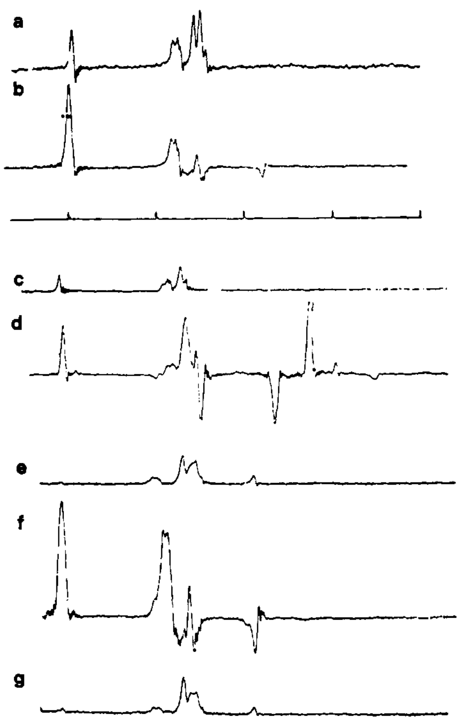


Figure 1. (a) Nmr spectrum (at 60 MHz) of benzaldehyde dissolved in perdeuteriobenzene at 25°, before irradiation. The field increases from left to right, and the separation between markers given below is 100 Hz. This spectrum is a time average of 12 scans. (b) Time-averaged (2 scans) spectrum of the same solution used for (a), during irradiation. (c) Time-averaged (3 scans) spectrum of benzaldehyde dissolved in CCl_4, before irradiation. (d) Time-averaged (3 scans) spectrum of the same sample used for (c), during irradiation. (e) Time-averaged (2 scans) spectrum of benzoin dissolved in perdeuterobenzene, obtained before irradiation. (f) Time-averaged (2 scans) spectrum of the same solution, during irradiation. (g) Time-averaged (2 scans) spectrum of the same sample, after irradiation.

Finally, additional evidence in favor of the radical-pair mechanism was obtained in the following manner. If benzaldehyde forms an intermediate radical pair, the product should be benzoin. Therefore, since the polarization can occur only if the radical pair formation is reversible, the irradiation of a solution of benzoin should result in production of benzaldehyde with the aldehyde proton polarized. This polarization does occur as can be seen in Figures 1e and f which give the spectrum of benzoin in perdeuteriobenzene before

---

(4) M. Cocivera, unpublished results.

(5) W. Herkstroeter and G. Hammond, *J. Amer. Chem. Soc.*, **88**, 4769 (1966).

(6) A. A. Lamola and N. Turro in "Technique of Organic Chemistry," Vol. XII, A. Weissberger, Ed., John Wiley and Sons, New York, N. Y., 1969.

(7) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," John Wiley and Sons, New York, N. Y., 1966.

(8) As can be seen, the photolysis of benzaldehyde in CCl_4 gives rise to many more lines than the perdeuteriobenzene solution, indicating that CCl_4 takes part in the reaction. The details of this reaction are under investigation. For this communication we restrict our attention to the aldehyde proton resonance line.

(9) S. Winstein and F. H. Seubold, *J. Amer. Chem. Soc.*, **69**, 2916 (1947). These authors found that the peroxide-initiated decarbonylation of β-phenylisovaleraldehyde and isovaleraldehyde did not occur in CCl_4, but that high yields of the corresponding acyl chlorides and chloropsin were obtained. They interpreted the results in terms of the following sequence.

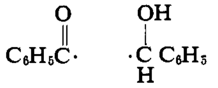
$$R\dot{C}O + ClCCl_3 \longrightarrow RCOCl + \cdot CCl_3$$
$$RCHO + \cdot CCl_3 \longrightarrow HCCl_3 + R\dot{C}O$$

and during optical irradiation, respectively. That the enhancement is quite large can be seen by comparing Figure 1f with Figure 1g which is the spectrum obtained after the sample has been irradiated for 2 min. All three spectra are time avaerages of two scans. Thus benzaldehyde is formed by the photolysis of benzoin, and the aldehyde protons are polarized. Furthermore, the nmr spectrum of benzaldehyde during irradiation (Figure 1b) is very similar to the nmr spectrum of benzoin during irradiation (Figure 1f). In fact, the chemical shift between the aldehyde proton line and the emission line that occurs at higher field is the same in both Figure 1b and f. Furthermore, this chemical shift is identical with the chemical shift between the aldehyde proton line and the lone line which occurs at the highest field in the normal nmr spectrum of benzoin (Figure 1e). We assign this line to the nonaromatic CH proton of benzoin. The structure of benzoin, labeled B, is given below.

The radical-pair mechanism which is consistent with these results is given in eq 2.[10] In this equation, A

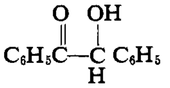
$$\begin{gathered} A \xrightarrow{h\nu} A^* \\ A^* + A \longrightarrow [D] \longrightarrow B \\ [D] \longrightarrow 2A \\ B \xrightarrow{h\nu} B^* \longrightarrow D \end{gathered} \qquad (2)$$

signifies the aldehyde, [D] signifies the radical pair, B signifies benzoin, and the asterisk signifies an excited molecule. [D] and B are shown below.[11] The radical pair is necessary to make the mechanism consistent with the fact that the enhancement of the aldehyde proton nmr line occurs as soon as irradiation is started. Out of necessity, some aspects of this mechanism have been left vague. For example, the benzaldehyde excited state which is involved in the dimerization has not been specified. At this point, we have no evidence to distinguish between the excited singlet and triplet states. Furthermore steps such as D → A* + A and D → B* have not been included since we have no evidence for them. However, they may occur, and we are studying this possibility. Finally, while the point in the mechanism at which the polarization occurs cannot be specified exactly, there are at least two possibilities. The polarization can occur in the radical pair itself or during its formation or dissociation. In the former case, the polarization would result from dynamic nuclear polarization, the Overhauser effect.[2] In the latter case, the polarization results because of the reaction. A number of workers[3,12,13] have obtained evidence for "reaction polarization"; however, its mechanism is still not completely understood.



$C_6H_5\overset{O}{\overset{\|}{C}}\cdot \quad \cdot\overset{OH}{\overset{|}{\underset{H}{C}}}C_6H_5$

[D]



$C_6H_5\overset{O}{\overset{\|}{C}}—\overset{OH}{\overset{|}{\underset{H}{C}}}C_6H_5$

B

In conclusion, we have used nmr and the nuclear polarizing effect of unpaired electrons to study the photolysis of benzaldehyde in solution at room temperature. The observed polarization of the aldehyde proton indicates that one of the photolytic processes involves a radical-pair intermediate. The other processes are currently under study.[13a]

---

[10] Other processes may be occurring also. For example, the photolysis of benzaldehyde may result in the formation of the phenyl radical. At the present time we are investigating this possibility.

[11] Closs observed nuclear polarization during the photoinduced reduction of benzophenone and concluded that the ketyl of benzophenone was involved in the polarization; see G. L. Closs and L. E. Closs, *J. Amer. Chem. Soc.*, **91**, 4550 (1969).

[12] H. R. Ward, R. G. Lawler, H. Y. Loken, and R. A. Cooper, *ibid.*, **91**, 4928 (1969).

[13] L. E. Closs and G. L. Closs, *ibid.*, **91**, 4549 (1969).

[13a] Note Added in Proof. In a personal communication to the authors, Dr. G. L. Closs has indicated that the results of his study of halogen-substituted benzaldehydes corroborate and elucidate further the mechanism proposed in this communication.

[14] Department of Chemistry, University of Guelph, Guelph, Ontario, Canada.

Michael Cocivera,[14] Anthony M. Trozzolo
Bell Telephone Laboratories
Murray Hill, New Jersey 07094

Received December 1, 1969

The Simultaneity of Allene Cycloadditions. II.[1] The Dimerization of Allene

Sir:

During the last couple of years there has been much speculation as to the mechanisms of (2 + 2) cycloaddition reactions of ketenes and allenes. This has largely been motivated by the statements of Woodward and Hoffmann[2] to the effect that, unlike other (2 + 2) cycloadditions, those of ketene and allene on theoretical grounds might very well be concerted. Indeed, Huisgen and others have gathered much experimental evidence in support of such a concerted pathway for many (2 + 2) cycloadditions of ketenes.[3]

The high stereoselectivity of a few (2 + 2) cycloadditions of allenic systems pointed toward the possibility that these reactions too were concerted.[4-6] Our recent studies on the secondary deuterium isotope effects of allene cycloadditions,[1] and those of Baldwin,[5] seem, however, to indicate that at least those reactions which we have investigated are nonsynchronous processes; that is, they pass through *two* transition states, the first of which apparently does not discriminate appreciably isotopically, and the second of which shows a significant secondary deuterium isotope effect.[7]

Nevertheless, the very interesting recent work of Moore and coworkers,[6] on the quite stereoselective dimerization of optically active 1,2-cyclononadiene, has been put forward, speculatively, by Hoffmann[9] as a possible example of a *concerted* (2 + 2) cycloaddition of

---

[1] Part I: W. R. Dolbier and S. H. Dai, *J. Amer. Chem. Soc.*, **90**, 5028 (1968).

[2] R. Hoffmann and R. B. Woodward, *Accounts Chem. Res.*, **1**, 17 (1968), and unpublished results.

[3] R. Huisgen and L. A. Feiler, *Chem. Ber.*, **102**, 3391 (1969), and following papers.

[4] E. F. Kiefer and M. Y. Okamura, *J. Amer. Chem. Soc.*, **90**, 4187 (1968).

[5] J. E. Baldwin, Abstracts, 157th National Meeting of the American Chemical Society, Minneapolis, Minn., April 1969, ORGN 003; J. E. Baldwin and U. V. Roy, *Chem. Commun.*, 1225 (1969), and personal communication.

[6] W. R. Moore, R. D. Bach, and T. M. Ozretich, *J. Amer. Chem. Soc.*, **91**, 5918 (1969). We thank Dr. Moore for communicating his results to us prior to publication.

[7] In the (2 + 2) cycloaddition of 1,1-dideuterioallene to both acrylonitrile and 1,1-dichloro-2,2-difluoroethylene, significant *intra*molecular secondary deuterium isotope effects were detected, but intermolecular effects were found to be very small, if not negligible.[1,5,8]

[8] S. H. Dai, Masters Thesis, University of Florida, Gainesville, Fla., 1969.

[9] R. Hoffmann, Abstracts, 21st National Organic Chemistry Symposium of the American Chemical Society, Salt Lake City, Utah, June 1969, p 109.