

Figure 2. ESR spectrum of CH_3AlH formed after 120-min photolysis of Al atoms at 368 nm (8 nm fwhm) in neat methane at 12 K. Stick diagrams indicate the position of the aluminum hyperfine components associated with the three principal g tensor axes, of which g_2 and g_3 are nearly coincident. Inserts show examples of superhyperfine splitting due to ^{13}C and ^2H nuclei in $^{13}\text{CH}_4$ and CD_4 matrices, respectively. Lines due to aluminum atoms remaining after photolysis are marked with an asterisk. Note also the presence of lines due to CH_3 radicals present on deposition and trace amounts of H atoms formed during photolysis.

formed from traces of O_2 impurity present on deposition and do not increase in intensity during any of the subsequent photolysis. No evidence for hydrogen atoms or AlH was seen on deposition in the ESR and IR spectra, respectively, which confirms that CH_3 is not being formed by an H atom abstraction by Al atoms. Photolysis at 368 or 305 nm resulted in the disappearance of the Al atom lines, while those associated with a product were seen to grow in (Figure 2). The product spectrum corresponds to that of an orthorhombic molecule, displaying single aluminum atom hyperfine and single proton superhyperfine splittings. Spectra recorded after photolysis of Al atoms in CD_4 and $^{13}\text{CH}_4$ matrices showed superhyperfine splittings due to one ^2H and one ^{13}C nucleus, respectively (Figure 2 inserts), thereby identifying the product as methyl aluminum hydride, CH_3AlH . The nonlinear geometry of this molecule is evident from the appearance of a 1:2:2:1 deuterium superhyperfine splitting (SHFS) pattern on g_2 and g_3 Al hyperfine lines (Figure 2, middle insert). This pattern arises from two overlapping 1:1:1 deuterium SHFS patterns of the g_2 and g_3 Al hyperfine components. If the product were axial, one would expect a single 1:1:1 triplet pattern. Broad-band photolysis above 400 nm caused the CH_3AlH ESR lines to disappear with a corresponding growth of Al atoms. Recovery yields of Al atoms were similar to those of UV-visible studies (vide infra), being greater than 80%.

These results indicate that a thermally-induced ground-state reaction of Al atoms with methane does not occur to any appreciable extent and that an efficient and reversible photochemical reaction, $\text{Al} + \text{CH}_4 \rightleftharpoons \text{CH}_3\text{AlH}$, is the only significant reaction pathway involving methane in this system under atomic Al conditions. It is conceivable that CH_3AlH arises from a photoactivated ground-state reaction, in which the barrier for the $\text{Al}(^2\text{P}) + \text{CH}_4$ reaction is surmounted by electronic to vibrational energy transfer from the photolytically generated $\text{Al}(^2\text{S})$ state to methane. This is anticipated as the $\text{Al}(^2\text{S}) + \text{CH}_4$ interaction is likely to be repulsive.⁷ We suggest that the previously reported ground-state reaction-product IR spectrum¹ is probably due to either reaction of methane with an aluminum oxide impurity or an extraneous reaction occurring in the furnace during sample preparation. A complete study of this system, including detailed

analysis of the electronic, vibrational, and ESR spectra of the various isotopically substituted product molecules will be reported in a forthcoming paper.

Note Added in Proof: Recent results show that Al atoms occupy two distinct sites in methane, with UV absorptions at 368, 310, and 303 nm (major site) and 348, 308, and 295 nm (minor site). Narrow band photolysis (8 nm fwhm) of Al atoms at either 368 or 348 nm gives rise to CH_3AlH in different sites as manifest by two separately occurring Al-H stretching mode frequencies at 1746 or 1764 cm^{-1} and by the observation of small shifts in the ESR spectral line positions. Wide band photolysis (20 nm fwhm) at either 305 or 368 nm causes simultaneous reaction of Al in both sites.

Effect of Solvent and Salts on Ion Pair Energies in the Photoreduction of Benzophenone by DABCO

Joshua L. Goodman and Kevin S. Peters*

Department of Chemistry, University of Colorado
Boulder, Colorado 80309

Received June 17, 1985

In recent years there has been an interest in organic ion pairs as reactive intermediates in photochemical reactions.¹ One difficulty encountered in mechanistic investigations is determining the energetics of ion pairs and how the energetics are influenced by the medium. Although the Rehm-Weller equation² has been useful for estimating the energetics of organic ion pairs in polar solvents, there is no general method that can be employed to determine the energetics of organic ion pairs in nonpolar solvents or in ionic media where specific salt interactions may occur.³ This is due in part to the lack of experimental data relating to medium effects upon organic ion pair energetics. In this report, we present the application of time-resolved photoacoustic calorimetry as a method for determining the effect of the medium upon ion pair energetics. Specifically, we examine the energetics of the ion pair formed in the photochemical reduction of benzophenone (Bz) by 1,4-diazabicyclo[2.2.2]octane (DABCO) and how the energetics are affected by the presence of added salts.

Laser excitation of benzophenone in the presence of DABCO, in acetonitrile, results first in the rapid formation (<25 ps) of the solvent-separated ion pair, SSIP, by electron transfer, and then collapse (~100 ps) to the amine contact ion pair, ACIP, Scheme I.⁴ In ethanol, hydrogen bonding of the SSIP prevents the collapse to the ACIP.⁵ In the presence of alkali metal cations, Li^+ and Na^+ , rapid ion pair exchange occurs in acetonitrile to form the alkali metal contact ion pair, MCIP.⁶ At high alkali metal salt concentrations (>0.1 M), the ratio of MCIP to ACIP is large (>10).⁶

The solvent and salt dependence for the ion pair energetics was determined by time-resolved photoacoustic calorimetry.⁷⁻⁹ The

(1) (a) Caldwell, R. A.; Creed, D. *Acc. Chem. Res.* **1980**, *13*, 45. (b) Lewis, F. D. *Acc. Chem. Res.* **1979**, *12*, 152. (c) Simon, J. D.; Peters, K. S. *Acc. Chem. Res.* **1984**, *17*, 277.

(2) (a) Rehm, D.; Weller, A. *Isr. J. Chem.* **1970**, *8*, 259. (b) Rehm, D.; Weller, A. *Ber. Bunsenges. Phys. Chem.* **1969**, *73*, 839, 849. (c) Knibbe, H.; Rehm, D.; Weller, A. *Ber. Bunsenges. Phys. Chem.* **1968**, *72*, 257.

(3) (a) Raber, D. J.; Harris, J. M.; Schleyer, P. v. R. In "Ions and Ion Pairs in Organic Reactions"; Vol. II, Szwarc, M., Ed.; Wiley: New York, 1983; Vol. II, pp 247-374. (b) McCullough, J. J.; Yeroushalmi, S. *J. Chem. Soc.* **1983**, 254. (c) Kitamura, N.; Imabayashi, S.; Tazuke, S. *Chem. Soc. Jpn. Chem. Lett.* **1983**, 455. (d) Goodson, B.; Schuster, G. B. *J. Am. Chem. Soc.* **1984**, *106*, 7254. (e) Goodman, J. L.; Peters, K. S., unpublished results.

(4) Simon, J. D.; Peters, K. S. *J. Am. Chem. Soc.* **1981**, *103*, 6403.

(5) Simon, J. D.; Peters, K. S. *J. Am. Chem. Soc.* **1982**, *104*, 6542.

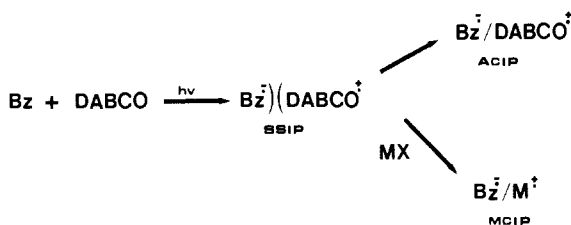
(6) Simon, J. D.; Peters, K. S. *J. Am. Chem. Soc.* **1983**, *105*, 4875.

(7) Rudzki, J.; Goodman, J. L.; Peters, K. S. *J. Am. Chem. Soc.* **1985**, *107*, 7849.

(8) Benzophenone was recrystallized from ethanol. DABCO was vacuum sublimed. The salts were dried under vacuum. Spectrograde solvents were used as received. Solutions (~0.2 OD) were degassed with argon for 10 min and then maintained under an argon atmosphere during experiment. Photolysis was initiated N₂ laser (337 nm, 5 ns, ≤20 μJ). Sample absorbances did not change during the experiment.

(7) Breckenridge, W. H. In "Reactions of Small Transient Species"; Fontijn, A., Clyne, M. A. A., Eds.; Academic Press: London, 1983.

Scheme I

Table I. Heats of Reaction of the Photoreduction of Benzophenone by DABCO^a

solvent	added salt	ΔH_r , ^b kcal/mol
acetonitrile	none	52.0
	LiClO ₄	46.7
	NaClO ₄	47.7
	(<i>n</i> -Bu) ₄ NClO ₄	52.0
ethanol	none	48.5

^a 337-nm excitation, ~0.2 OD, 0.1 M DABCO, 0.5 M salt, 298 K. ^b Values ± 1.0 kcal/mol, ΔH_r is the enthalpy difference between the corresponding ion pair and initial reactants.

ΔH_r , Table I, is determined by deconvolution of the photoacoustic waveform obtained from photolysis of the sample. The standard employed as the transducer wave was ferrocene.⁷ The ΔH_r values measured in acetonitrile correspond to the energy of the ACIP without added alkali metal salts and the MCIP with added alkali metal salts.¹⁰ The energy of the hydrogen bonded ion pair is given by ΔH_r in ethanol.¹¹

The energies of the ion pairs in acetonitrile are ordered, $E(\text{Li}^+) < E(\text{Na}^+) < E((n\text{-Bu})_4\text{N}^+) \approx E(\text{no salt})$, Table I. The lower energies of the Na⁺ and Li⁺ ion pairs are not due to an increase in ionic strength but rather to specific ionic interactions because the addition of the nonassociating salt (*n*-Bu)₄NClO₄ did not lower the energy of the ACIP.¹² The difference of only 1 kcal/mol in the ion pair energies for Li⁺ and Na⁺ is somewhat surprising since normally Li⁺ is considered to bind more strongly, via Coulombic attraction, than Na⁺ due to the smaller ionic radius of Li⁺. However, the 1 kcal/mol does not reflect the absolute difference in binding between the two cations with the radical anion of benzophenone. Rather, these measurements reflect only the difference in binding energies of the cation with the organic anion and the solvent, acetonitrile.

The free energy change, ΔG , from ground-state reactants to the ACIP, can be estimated from the Rehm-Weller equation,²

$$\Delta G = 23.06(E_{1/2}^{\text{ox}} - E_{1/2}^{\text{red}}) - e^2/(\epsilon r)$$

where $E_{1/2}^{\text{ox}}$ is the oxidation potential of DABCO, $E_{1/2}^{\text{red}}$ is the reduction potential of benzophenone, ϵ is the dielectric constant of the medium, and r is the encounter distance of the ion pair. Redox potentials of DABCO and benzophenone were measured in acetonitrile,¹³ and the difference, $E^{\text{ox}} - E^{\text{red}} = 2.47$ eV, is in

(9) The volume change for a photochemical reaction, ΔV , may contribute to the observed acoustic wave. In this case, the negative ΔV of reaction would give a seemingly large value for ΔH_r . However, the volume change in organic solvents should not significantly increase the acoustic signal so the stated enthalpies should be an upper limit.

(10) The equilibrium structure of the perchlorate alkali metal salts in acetonitrile is the solvent-separated ion pair.⁶ Consequently, the enthalpy contribution to unpair the ions is believed to be small.

(11) On the time scale of the laser experiment, ~1 μs , decay of the ion pairs is slow and consequently does not contribute significantly to the overall enthalpy or reaction. However, deconvolution of the waveforms can be performed to account for this slow decay.⁷ The decays of the ACIP and the Na⁺ and Li⁺ ion pairs in acetonitrile are approximately 15, 20, and 30 μs , respectively.

(12) The lack of increased stabilization of the ACIP with the addition of (*n*-Bu)₄ClO₄ may be anticipated from the absence of any significant salt effect on solvolysis rates in acetonitrile, i.e., small b value.^{3a}

(13) Cyclic voltammogram parameters at 298 K: ca. 10⁻³ M Bz, 10⁻³ M DABCO, 0.2 M TBABF₄ in CH₃CN, vs. Ag/AgNO₃ (0.1 M), TBABF₄ (0.5 M). Sweep rate from 50 to 1 V/s.

accord with literature values.¹⁴ By use of this difference, $\epsilon = 37.5$ ¹⁵ and $r = 2.9$ Å,¹⁶ the above equation gives $\Delta G \approx 54$ kcal/mol. The calculated and experimental heats of reaction are in good agreement if the entropy of formation of the ion pair is small.¹⁷ Similarly, in ethanol, using $E^{\text{ox}} - E^{\text{red}} = 2.17$ eV from literature redox potentials,¹⁸ $\Delta G \approx 50$ kcal/mol which agrees well with the experimental value.¹⁹

The reasonable agreement between the calculated and experimental values suggests that the term $e^2/(\epsilon r)$ is small and, in particular, that ϵ is large. Consequently, the argument that the macroscopic dielectric constant at large r decreases to the square of the index of refraction as r becomes small appears invalid when applied to the above Rehm-Weller equation.²⁰

In summary, quantitative measurements of the stabilizing effect of alkali metals and the consequent driving force for the formation of the MCIP in the photoreduction of benzophenone have been determined by photoacoustic calorimetry. In addition, the experimental enthalpies support the use of the Rehm-Weller equation to estimate the ion pair energies of the ACIP.

Acknowledgment. This work was supported by the NSF (CHE-8418611). K.S.P. acknowledges support from the Alfred P. Sloan Foundation and the Henry and Camille Dreyfus Foundation for a teacher-scholar grant. J.L.G. acknowledges generous support from an NIH postdoctoral fellowship. We thank Prof. C. Koval for conducting the electrochemical measurements.

Registry No. Bz, 119-61-9; DABCO, 280-57-9.

(14) (a) McKinney, T. M.; Geske, D. H. *J. Am. Chem. Soc.* **1965**, *87*, 3013. (b) Loutfy, R. O.; Loutfy, R. O. *J. Phys. Chem.* **1973**, *77*, 336.

(15) Reichardt, C. "Solvent Effects in Organic Chemistry"; Verlag Chemie: New York, 1979; p 270.

(16) Pauling, L. "Nature of the Chemical Bond"; Cornell University: Ithaca, NY, 1960.

(17) If we assume the entropy of formation, derived by Weller,^{2b} of an exciplex to be -18 eu as the upper limit, then the estimated ΔH_r value from the Weller equation is ~49 kcal/mol.

(18) (a) Smith, J. R.; Masheder, D. *J. Chem. Soc., Perkin Trans. 2* **1977**, 1732. (b) Kalinowski, M. K.; Grabowski, Z. R.; Pakula, B. *J. Chem. Soc., Faraday Trans.* **1966**, *62*, 918.

(19) In ethanol, the encounter distance of the hydrogen bonded ion pair is believed to be large, so the $e^2/(\epsilon r)$ term is negligible, i.e., ~0.

(20) Sadek, H.; Fuoss, R. M. *J. Am. Chem. Soc.* **1954**, *76*, 5905.

Mixed Valence, Phosphine Stabilized Sulfido Clusters of the Transition Metals: Synthesis and Structure of Cr₃(μ_3 -S)₂(μ_2 -S)₃(dmpe)₃, Cr(III,III,IV) (dmpe = Bis(1,2-dimethylphosphino)ethane). A Structurally Characterized Cr₃ Cluster

Atta M. Arif, John G. Hefner, and Richard A. Jones*

Department of Chemistry, The University of Texas at Austin, Austin, Texas 78712

Thomas A. Albright* and Sung-Kwon Kang

Department of Chemistry, The University of Houston Houston, Texas 77004

Received September 3, 1985

The relevance of complexes containing transition-metal-sulfur bonds to biological systems¹ as well as to industrially important

(1) Newton, W. E.; Otsuka, S., Eds. "Molybdenum Chemistry of Biological Significance"; Plenum Press: New York, 1980. Lovenberg, W., Ed. "Iron-Sulfur Proteins"; Academic Press: New York, 1973, Vol. 1; 1974, Vol. 2; 1976, Vol. 3. Stiefel, E. I. *Prog. Inorg. Chem.* **1977**, *22*, 1; *Proc. Natl. Acad. Sci. U.S.A.* **1973**, *70*, 988. Shah, V. K.; Brill, W. J. *Proc. Natl. Acad. Sci. U.S.A.* **1977**, *74*, 3249. Coucouvanis, D. *Acc. Chem. Res.* **1981**, *14*, 201. Eisenberger, P.; Kinkaid, B. M. *Science (Washington, D.C.)* **1978**, *200*, 1441. Sola, T.; Do, Y.; Berg, T. M.; Holm, R. H. *J. Am. Chem. Soc.* **1983**, *105*, 7784. Do, Y.; Simhon, E. D.; Holm, R. H. *J. Am. Chem. Soc.* **1983**, *105*, 6731. Draganjac, M.; Coucouvanis, D. *J. Am. Chem. Soc.* **1983**, *105*, 139.