the limit of experimental uncertainties. Since vibrational Raman spectra are sensitive to the molecular conformation, the coincidence of the spectra in Figure 1A, B indicates that the same T_1 conformer of SA is produced by the photoexcitation of the cis and trans molecules. Then the photochemical results show that this triplet species of SA is not in a perpendicular conformation but in a trans conformation which exclusively relaxes into *trans*-SA in the ground state (otherwise the reverse trans to cis isomerization should occur and the quantum chain process should not take place).

The assignment of the observed T_1 spectrum to a trans structure may further be supported by the following discussion. The $T_n \leftarrow T_1$ absorption spectrum of SA exhibits two prominent peaks at 460 and 620 nm.[4] The former resembles the 420-nm band of anthracene and is assigned to a transition mostly localized to the anthracene moiety. The latter is most probably due to a transition extending over the whole molecule including the central C=C part. The Raman excitation at 612 nm is therefore expected to resonantly enhance the intensities of the olefinic vibrations as well as the aromatic ring modes. In fact, the T_1 spectrum of SA in Figure 1 is quite different from that of T_1 anthracene[5] but possesses some similarities with the S_1 Raman spectrum of *trans*-stilbene,[6,7] which is the only known vibrational spectrum of an aromatic olefin in a $\pi^*\pi$ excited electronic state. The bands at 1550, 1243, and 1174 cm^{-1} correspond well with the three major peaks of S_1 *trans*-stilbene spectrum, 1565 (C=C stretch), 1241 (olefinic CH ip bend), and 1179 cm^{-1} (C-phenyl stretch + ring modes). It is not surprising that we have such similarities. A stilbene frame is involved in the central part of SA and the vibrational modes localized to this part are likely to be common to T_1 SA and S_1 *trans*-stilbene provided that these two species have similar geometries around the C=C double bond. The Raman spectrum of T_1 SA is thus consistent with a trans structure which is well established for S_1 *trans*-stilbene.[8]

In this way, information obtained in the present study firmly supports the idea of "one-way" photoisomerization.

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Photochemical Activation of Methane by Aluminum Atoms: Al + $CH_4 \rightleftarrows CH_3AlH$, a Photoreversible Reaction

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The recently reported ground-state insertion of aluminum atoms into the C-H bond of methane at 10 K[1] is of great importance with respect to the understanding of the activation of methane by single metal atoms.[2] We have investigated the Al/CH_4 system and have found no evidence for a thermally induced ground-state reaction but find the photochemically induced reaction to be both facile and photoreversible.

Figure 1A shows the UV-visible spectrum of Al atoms (vaporized from a tantalum filament) isolated in neat methane at 12 K before photolysis. The deposition spectrum is very similar to that reported for Al atoms in Ar, Kr, Xe matrices[3] except for the expected matrix shifts and the presence of two trapping sites in methane, indicating that the atoms are in a relatively unperturbing and unreactive environment. The main features are those associated with the $^2D \leftarrow {}^2P$ (310, 308, 303, 295 nm) and $^2S \leftarrow {}^2P$ (368, 348 nm) resonance transitions of Al atoms. Photolysis at 368 or 305 nm[4] (20-nm fwhm) resulted in rapid depletion of all features associated with Al atoms while giving rise to a broad absorption between 450 and 600 nm (Figure 1B). Subsequent broad-band photolysis above 400 nm resulted in the disappearance of the 450-600-nm band and a recovery of about 80% of the Al atoms initially present with no other products detected (Figure 1C), demonstrating the existence of an efficient photoreductive-elimination pathway. During the primary photolysis at 305 nm some growth of Al_2 (400, 283 nm)[3,5] was observed, indicating that photoaggregation is a competing pathway, probably accounting for a 20% loss of the Al atoms at most.

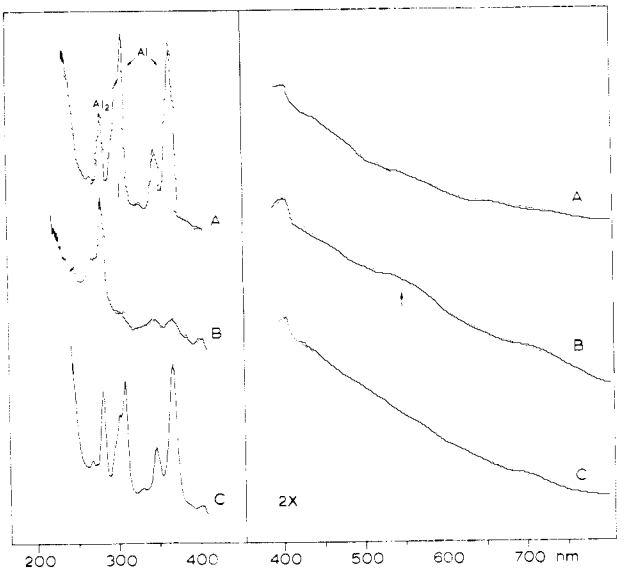

Figure 1. UV-visible spectra of Al atoms isolated in neat methane at 12 K (A) on deposition, (B) after 90-min photolysis at 305 nm, and (C) after subsequent broad-band photolysis for 2.5 h above 400 nm.

Infrared studies of the photochemistry of Al atoms in methane were also performed. The deposition spectra showed no features attributable to a ground-state insertion reaction product, and the bands reported by Klabunde[1] as being present on deposition and due to CH_3AlH were not observed. Subsequent photolysis at the 368- or 305-nm aluminum atom absorptions gave rise to spectra which were similar to that suggested by Klabunde to be due to secondary reaction products. Product absorptions were observed at 1764 (w), 1746 (s), 1162 (w), 730 (m), 610 (w), and 470 (w) cm^{-1} and are consistent with those expected for methyl aluminum hydride in which the molecule occupies two distinct trapping sites. The product was stable under prolonged photolysis at 368 or 305 nm. In contrast, broad-band photolysis above 400 nm caused these product bands to disappear completely without any new IR bands appearing.

The ESR spectrum of Al atoms (^{27}Al, 100%, $I = {}^5/_2$) isolated in neat methane was recorded and is similar to that reported for Al atoms isolated in rare gas matrices.[6] Hyperfine features associated with atomic aluminum were accompanied by reasonably intense bands due to methyl radicals. These bands probably originate from cracking of methane by an Al-containing species

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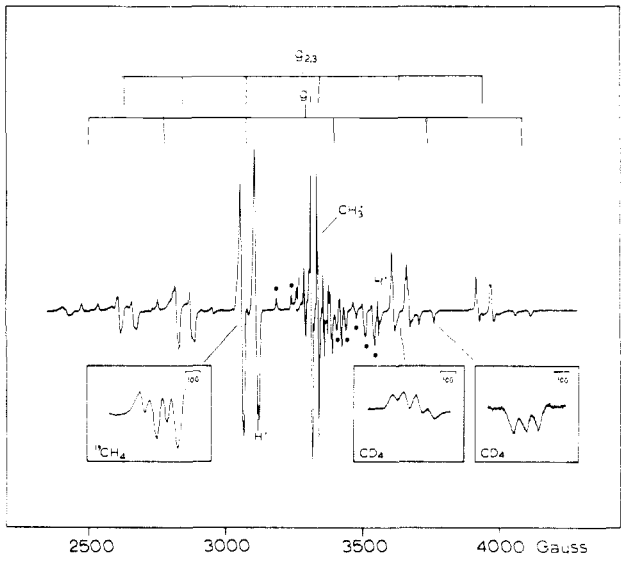

Figure 2. ESR spectrum of CH_3AlH formed after 120-min photolysis of Al atoms at 368 nm (8 nm fwhm) in neat methane at 12 K. Stick diagrams indicate the position of the aluminum hyperfine components associated with the three principal g tensor axes, of which g_2 and g_3 are nearly coincident. Inserts show examples of superhyperfine splitting due to ^{13}C and ^2H nuclei in $^{13}CH_4$ 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 depostion 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 $^{13}CH_4$ 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, $Al + CH_4 \rightleftarrows CH_3AlH$, 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 $Al(^2P) + CH_4$ reaction is surmounted by electronic to vibrational energy transfer from the photolytically generated $Al(^2S)$ state to methane. This is anticipated as the $Al(^2S) + CH_4$ interaction is likely to be repulsive.[7] We suggest that the previously reported ground-state reaction-product IR spectrum[1] 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.

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

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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 equation[2] 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

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(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 N_2 laser (337 nm, 5 ns, ≤20 μJ). Sample absorbances did not change during the experiment.

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