increases glucagon potency in both the binding and adenylate cyclase assays.

Acknowledgment. This research was supported by a grant for the U.S. Public Health Service AM 21085 and in part by a grant from Merck Sharp and Dohme. V.J.H. is a recipient of a Guggenheim Fellowship, 1984-1985.

Transient Raman Evidence of the "One-Way" Cis to Trans Isomerization in the Lowest Excited Triplet State of 2-Styrylanthracene

Hiro-o Hamaguchi,*[†] Mitsuo Tasumi,[†] Takashi Karatsu,[‡]
Tatsuo Arai,[‡] and Katsumi Tokumaru*[‡]

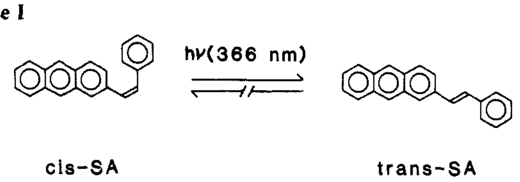
Department of Chemistry, Faculty of Science
The University of Tokyo, Bunkyo-ku, Tokyo 113, Japan
Department of Chemistry, University of Tsukuba
Sakura-mura, Ibaraki 305, Japan

Received April 15, 1985

Elucidation of the mechanism of the cis-trans photoisomerization of olefins and related compounds has long been one of the central problems of photochemistry. The generally accepted scheme of photoisomerization assumes the so-called perpendicular excited singlet or triplet species as the key intermediate. Isomerization takes place after this species is diabatically converted to the perpendicular ground state which finally gives a mixture of the cis and trans isomers.[1] Recently, we found that this scheme is not applicable to the isomerization through the lowest excited triplet (T_1) states of some aromatic and conjugated polyene compounds. The direct and triplet-sensitized irradiation of 1-(2-anthryl)-3,3-dimethyl-1-butene in benzene resulted in a 100% "one-way" cis to trans isomerization.[2] The quantum yield for the cis to trans conversion far exceeded unity, implying a quantum chain process involving a long-lived intermediate that is most likely the trans T_1 species. From the observed nanosecond transient Raman spectra, it was proved that the photoexcitation of the 7-cis, 9-cis, and 11-cis isomers of retinal in hexane gave the same T_1 isomer as that produced from the all-trans form.[3] Similar results were obtained from the $T_n \leftarrow T_1$ absorption spectra of a group of anthrylethylenes.[4] In order to account for these photochemical and spectroscopic findings, we proposed a novel adiabatic isomerization mechanism in which the initially resulting cis T_1 species undergoes a rapid relaxation to the trans which is located at an energy minimum on the T_1 potential surface.

It seems important, at this stage, to focus our attention to the study of a simple prototypical molecule so that we are able to establish the concept of "one way" photoisomerization. In this paper, we wish to present new direct evidence that is based on transient Raman spectroscopy of 2-styrylanthracene (Scheme I; hereafter abbreviated as SA) and that is supported also by the photochemical data. Our transient Raman evidence is 2-fold. First, the same T_1 conformer is produced either from *trans*- or *cis*-SA by the photoexcitation, and, second, the Raman spectrum of this species is consistent with a trans structure.

Scheme I



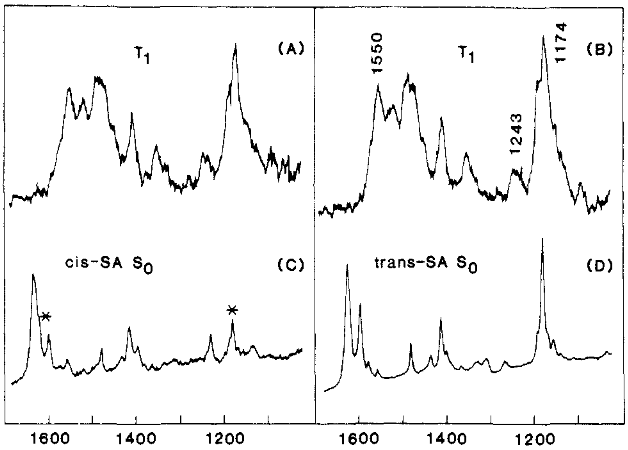


Figure 1. Transient T_1 Raman spectra obtained from benzene solutions of *cis*-SA (A) and *trans*-SA (B) and S_0 Raman spectra of crystalline *cis*-SA (C) and *trans*-SA (D). Asterisks in spectrum (C) mark the bands that might have small contributions from the trans molecules which were produced by the laser irradiation during the measurement.

The samples of *cis*- and *trans*-SA were prepared and purified as reported previously.[4] Transient resonance Raman spectra were obtained by using the third harmonic (355 nm, 10-Hz repetition, 5-ns pulsewidth) of a Q-switched Nd:YAG laser (Quanta-Ray DCR-2A) for pumping and the R-610 dye output (612 nm, 10 Hz, 5 ns) from a pulsed dye laser (Quanta-Ray PDL-1) for Raman probing. The probing pulse was delayed about 20 ns from the pumping pulse to avoid the interference from fluorescence. These two laser beams were spatially superimposed on a thin-film jet of the sample solution ($(1-2) \times 10^{-3}$ M in spectroscopic-grade benzene). The Raman scattered light was analyzed with a polychromator (Spex 1877) and detected with a gated (5 ns) intensified photodiode array detector (PAR 1420 and 1218). The spectral data were transferred to a minicomputer (DEC MINC-11) and processed. HPLC analysis of the sample solution showed that less than 10% of the *cis*-SA molecules photoisomerized during the Raman measurements. Raman spectra of crystalline SA in the ground state (S_0) were measured by using a He-Ne laser as the exciting source.

It is already reported that *cis*-SA undergoes a 100% "one-way" isomerization to trans upon the direct photoexcitation at 366 nm (Scheme I).[4] In order to confirm that the isomerization takes place in the T_1 manifold and not in the S_1, both the direct and biacetyl (0.1 M) sensitized irradiation of *cis*-SA in deaerated benzene were performed at room temperature for various concentrations ranging from 1.31×10^{-4} to 1.57×10^{-3} M. In both cases, the observed quantum yield $\Phi_{c \to t}$ increased linearly with the concentration [*cis*-SA]; $\Phi_{c \to t} = \Phi_{ISC}(1 + k_q\tau_T[cis\text{-SA}])$, where Φ_{ISC} is the intersystem crossing quantum yield either for SA (direct irradiation) or for biacetyl (sensitized irradiation), k_q, the rate constant for the energy transfer from trans T_1 to cis S_0 giving cis T_1 to accomplish the quantum chain process, and τ_T, the lifetime of trans T_1 (190 μs in benzene at room temperature[4]). The value of $\Phi_{c \to t}$ was 6.8 and 17.8 at 1.57×10^{-3} M of [*cis*-SA] on the direct and sensitized irradiation, respectively, showing that the quantum chain process took place. The constant $k_q\tau_T$ was determined as 9.8×10^3 M^{-1} for the direct and 1.1×10^4 M^{-1} for the sensitized irradiation. Agreement between these two $k_q\tau_T$ values shows that the isomerization indeed occurs in the T_1 manifold.

The T_1 resonance Raman spectra and S_0 Raman spectra of *cis*- and *trans*-SA are shown in Figure 1. The two S_0 spectra (Figure 1C,D) are markedly different from each other, especially in the 1100-1300-cm^{-1} region where conformation-sensitive bands are located. On the other hand, T_1 spectra obtained from *cis*-SA (Figure 1A) and from *trans*-SA (Figure 1B) are identical within

---

[†] The University of Tokyo.

[‡] University of Tsukuba.

(1) (a) Hammond, G. S.; Saltiel, J.; Lamola, A. A.; Turro, N. J.; Bradshaw, J. S.; Cowan, D. O.; Counsell, R. C.; Vogt, V.; Dalton, C. *J. Am. Chem. Soc.* **1964**, *86*, 3197. (b) Schulte-Frohlinde, D.; Görner, H. *Pure Appl. Chem.* **1979**, *51*, 279. (c) Saltiel, J.; Marchand, G. R.; Kirkor-Kaminska, E.; Smothers, W. K.; Mueller, W. B.; Charton, J. L. *J. Am. Chem. Soc.* **1984**, *106*, 3144.

(2) Arai, T.; Karatsu, T.; Sakuragi, H.; Tokumaru, K. *Tetrahedron Lett.* **1983**, *24*, 2873.

(3) Hamaguchi, H.; Okamoto, H.; Tasumi, M.; Mukai, Y.; Koyama, Y. *Chem. Phys. Lett.* **1984**, *107*, 355.

(4) Karatsu, T.; Arai, T.; Sakuragi, H.; Tokumaru, K. *Chem. Phys. Lett.* **1985**, *115*, 9.

0002-7863/86/1508-1698$01.50/0

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.

---

[5] Beck, S. M.; Brus, L. E. *J. Chem. Phys.* **1981**, *75*, 1031.
[6] Gustafson, T. L.; Roberts, D. M.; Chernoff, D. A. *J. Chem. Phys.* **1983**, *79*, 1559.
[7] Hamaguchi, H.; Kato, C.; Tasumi, M. *Chem. Phys. Lett.* **1983**, *100*, 3. Hamaguchi, H.; Urano, T.; Tasumi, M. *Chem. Phys. Lett.* **1984**, *106*, 153.
[8] See, for example: Warshel, A. *J. Chem. Phys.* **1975**, *62*, 214.

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

J. Mark Parnis and Geoffrey A. Ozin*

Department of Chemistry, University of Toronto
Toronto, Ontario, Canada M5S 1A1

Received September 9, 1985

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.

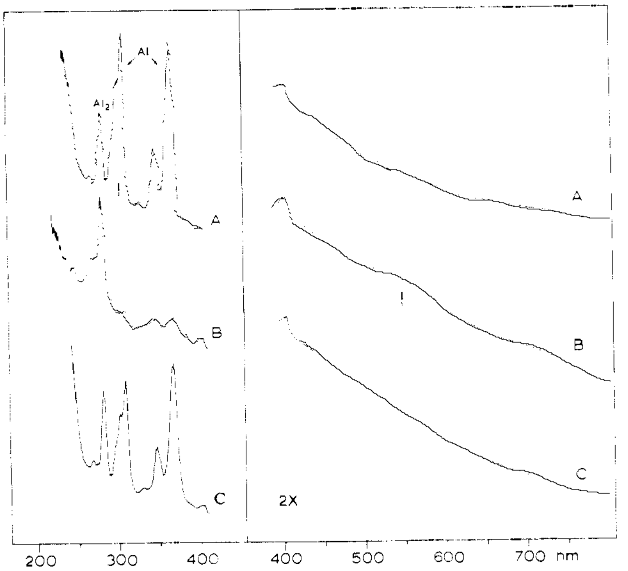


Figure 1. UV-visible spectra of Al atoms isolated in neat methane at 12 K (A) on deposition, (B) after 90-min photolysis at 305 nm, and (C) after subsequent broad-band photolysis for 2.5 h above 400 nm.

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

---

[1] Klabunde, K. J.; Tanaka, Y. *J. Am. Chem. Soc.* **1983**, *105*, 3544–3546.
[2] Billups, W. E.; Konarski, M. M.; Hauge, R. H.; Margrave, J. L. *J. Am. Chem. Soc.* **1980**, *102*, 7394–7396. Ozin, G. A.; McIntosh, D. F.; Mitchell, S. A.; Garcia-Prieto, J. *J. Am. Chem. Soc.* **1981**, *103*, 1574–1575. Ozin, G. A.; McCaffrey, J. G. *J. Am. Chem. Soc.* **1982**, *104*, 7351–7352. Ozin, G. A.; McCaffrey, J. G.; McIntosh, D. F. *Pure Appl. Chem.* **1984**, *56*, 111–128. Breckenridge, W. H.; Umemoto, H. *J. Chem. Phys.* **1984**, *81*, 3852–3865. Breckenridge, W. H.; Renlund, A. M. *J. Phys. Chem.* **1979**, *83*, 1145–1150.
[3] Abe, H.; Kolb, D. M. *Ber. Bunsenges. Phys. Chem.* **1983**, *87*, 523–527.
[4] The photolysis source used in this study consisted of a 450-W Xe arc lamp (Osram) in an Oriel housing coupled to a 10-cm water-filled IR filter cell and an Oriel 7240 monochromator, delivering 50–100 μW cm^{-2} at the sample.
[5] Douglas, M. A.; Hauge, R. H.; Margrave, J. L.; *J. Phys. Chem.* **1983**, *87*, 2945.
[6] Knight, L. B.; Weltner, W. *J. Chem. Phys.* **1971**, *55*, 5066–5077.

0002-7863/86/1508-1699$01.50/0