

The crystal structure determination⁸ shows that (CpTi)₅S₆ contains sulfur bridging the triangular faces of a distorted trigonal bipyramid of titanium atoms (Figure 1). The distortion takes the form of a displacement of one of the equatorial titanium atoms (Ti(4) in Figure 1) away from one other equatorial titanium (Ti(1)) and toward an axial titanium (Ti(5)). The distance Ti(4)-Ti(1) is 3.214 (5) Å, Ti(4)-Ti(5) is 3.076 (5) Å, and the average for all other Ti-Ti distances is 3.160 (5) Å with a range from 3.145 (5) to 3.173 (5) Å. All the Ti-Ti distances are longer than those of (CpTi)₆O₈ (average Ti-Ti 2.891 (1) Å²) because of the larger covalent radius of sulfur (1.02 Å) vs. oxygen (0.73 Å); (CpV)₅O₆ is an essentially perfect trigonal bipyramid with V-V distances ranging from 2.738 (3) to 2.762 (2) Å.¹

The new cluster is paramagnetic, as would be expected for a species with an odd number of electrons. The ESR spectrum (toluene solution) shows a single line at $g = 1.993$ with weak satellites attributable to hyperfine interaction with the Ti isotopes (Figure 2). The spectrum at -80 °C is essentially identical with that at 20 °C, though the satellites are not observed at the lower temperature. The bulk magnetic susceptibility per mole at 20 °C is 6.525×10^{-4} . This corresponds to a magnetic moment of 1.25 μ_B , which is low compared to the spin-only value for one electron of 1.73 μ_B due mainly to the lack of a diamagnetic correction for any of the ligands or titanium atoms.⁹ However, both the narrow line ESR spectrum and the bulk magnetic moment indicate the presence of one unpaired electron in (CpTi)₅S₆.

Both the distortion of (CpTi)₅S₆ and its one unpaired electron can be understood in terms of the theoretical model presented previously.³ The new cluster has three electrons to be accommodated in the 12 cluster orbitals. In a perfect trigonal-bipyramidal structure (D_{3h} symmetry) the electron configuration would be $(1a'_1)^2(1e')^1$. Therefore Jahn-Teller distortion of the D_{3h} structure is expected. Since both the $1a'_1$ and $1e'$ orbitals are almost completely localized on the equatorial titanium atoms, the distortion must involve these atoms, as is observed. The distortion is such that (CpTi)₅S₆ has no symmetry within experimental error.

Since the three cluster electrons are localized on the equatorial titanium atoms, one may naively consider each of these atoms to be Ti(III) (d^1) and the axial titanium atoms to be Ti(IV) (d^0). This assignment of oxidation states is in agreement with the observed Ti-S distances. The equatorial Ti-S distances average 2.474 (7) Å with a range from 2.443 (7) to 2.506 (7) Å; the axial Ti-S distances are much shorter, averaging 2.279 (7) Å with a range from 2.263 (8) to 2.308 (6) Å. The Ti-S distances may be compared to those in Cp*₂TiS₃ (Cp* = η^5 -C₅(CH₃)₅) and Cp₂TiS₃, 2.413 (4) Å^{10a} and 2.420 and 2.446 Å.^{10b} The Ti(4)-S distances are identical with those of the other equatorial titanium atoms (Ti(1)-S and Ti(3)-S); the trigonal pyramid of sulfur atoms is distorted with the trigonal bipyramid of titanium atoms in order to retain the Ti-S bonding. This is in accord with the theoretical model in which the 12 cluster orbitals of (CpM)₅A₆ are essentially pure metal orbitals and are nonbonding with respect to the M-A interaction.

Analogous reactions to those between Cp₂Ti(CO)₂ and H₂O or H₂S do not occur with Cp₂Zr(CO)₂ presumably because of the instability of the Zr(III) oxidation state. On reaction with H₂O,

Cp₂Zr(CO)₂ gives only ZrO₂ and with H₂S the product is the known⁷ complex (Cp₂ZrS)₂.

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Supplementary Material Available: Tables of atomic coordinates, thermal parameters, and bond lengths (7 pages). Ordering information is given on any current masthead page.

Excited-State Chemistry of Tetrakis(μ -pyrophosphito)diplatinum(II). Photoinduced Addition of Aryl Bromides and Iodides to the Binuclear Complex and the Photoinduced Catalytic Conversion of Isopropyl Alcohol into Acetone and Hydrogen

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Aqueous solutions of the binuclear platinum(II) complex Pt₂(μ -P₂O₅H₂)₄⁴⁺ show an intense absorption band at 367 nm (ϵ_{\max} 3.45×10^4) and a corresponding emission at 514 nm.¹ This emission has been identified as a long-lived phosphorescence ($\tau = 9.8$ (2) μ s) originating from a triplet excited state.² Using a simplified MO treatment, the respective ground- and excited-state configurations of these binuclear d⁸ complexes are represented as $(d_{z^2})^2(d_{x^2-y^2})^2$ and $(d_{z^2})^2(d_{x^2-y^2})^1(p_z)^1$. The excited state Pt₂(μ -P₂O₅H₂)₄⁴⁺* undergoes efficient energy quenching with SO₂.³ Quenching is also observed with electron-transfer reagents, and from experiments using different oxidants the electrode potential for Pt₂(μ -P₂O₅H₂)₄⁴⁺*/Pt₂(μ -P₂O₅H₂)₄³⁺ has been estimated to be < -1 V.⁴ This long microsecond lifetime for Pt₂(μ -P₂O₅H₂)₄⁴⁺* makes it conceptually feasible to carry out reaction chemistry with this triplet excited state, and its strong reducing properties makes it a useful reagent for reaction with organic halides. This paper reports the first organometallic reactions of Pt₂(μ -P₂O₅H₂)₄⁴⁺* and relates its redox behavior and radical character to the Gray MO model.

The complex Pt₂(μ -P₂O₅H₂)₄⁴⁺ undergoes thermal addition of halogens X₂ and methyl iodide to give the axially disubstituted Pt(III)-Pt(III) complexes Pt₂(μ -P₂O₅H₂)₄X₂⁴⁺ and Pt₂(μ -P₂O₅H₂)₄MeI⁴⁺.⁵ Thermal addition of the higher homologues RI (R = Et, *n*-Pr, *i*-Pr, *n*-pent) also gives Pt₂(μ -P₂O₅H₂)₄RI⁴⁺, but the complex is contaminated with Pt₂(μ -P₂O₅H₂)₄I₂⁴⁺.⁶ Aryl halides do not undergo thermal addition. Aryl bromides or iodides

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(8) Data for (C₅H₅)Ti₅S₆ ($M = 757.4$) were obtained from a wedge-shaped chip cut from a large irregular crystal and were measured on a Picker FACS-1 diffractometer. Space group $P2_1/n$, $a = 16.978$ (5) Å, $b = 17.008$ (9) Å, $c = 10.122$ (3) Å, $\beta = 92.44$ (2)°, $Z = 4$, $D_c = 1.72$, 1383 observed ($I > 3\sigma(I)$) reflections out of 3828 with $2\theta \leq 45^\circ$. The data were corrected for absorption and all atoms except H were refined anisotropically to a conventional R of 0.074, $R_w = 0.077$. The structure was solved by MULTAN80 and refined by SHELX. Tables of atomic positions, thermal parameters, and bond lengths are available as supplementary material. Attempts to obtain crystals that diffract better are continuing.

(9) Correction for the diamagnetism of 5C₅H₅⁻ ($-50.9 \times 10^{-6} \times 5$), 6S²⁻ ($-38 \times 10^{-6} \times 6$), 2Ti⁴⁺ ($-5 \times 10^{-6} \times 2$), and 3Ti³⁺ ($-9.2 \times 10^{-6} \times 3$) gives a moment of 1.66 μ_B . See: Weiss, A.; Witte, H. "Magnetochemie"; Verlag Chemie: Weinheim, 1973; pp 93-95.

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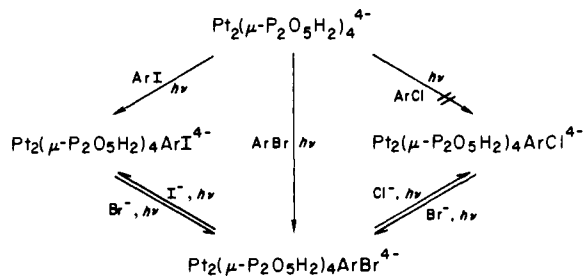
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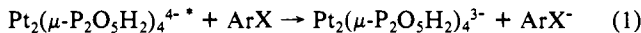
(6) UV-vis data for Pt₂(μ -P₂O₅H₂)₄RI⁴⁺: λ_{\max} 352 (R = Et); 355 nm (R = *i*-Pr, *n*-Pr, *n*-pent). UV-vis data for Pt₂(μ -P₂O₅H₂)₄X₂⁴⁺: λ_{\max} 338 (X = I), 305 nm (X = Br): from ref 5.

Scheme I



(ArX), but not aryl chlorides, will add to the excited state $\text{Pt}_2(\mu\text{-P}_2\text{O}_5\text{H}_2)_4^{4-*}$ to give the axially disubstituted complexes $\text{Pt}_2(\mu\text{-P}_2\text{O}_5\text{H}_2)_4\text{ArX}^{4-}$ (X = Br, I).⁷ Subsequent photoinduced substitution occurs with added halide ion Y^- (Y = Cl, Br, I) to give $\text{Pt}_2(\mu\text{-P}_2\text{O}_5\text{H}_2)_4\text{ArY}^{4-}$ (Scheme I). We believe this reaction is the first example of aryl halide addition to platinum(II). Usually the addition of aryl halides to platinum compounds only occurs with the electron-rich alkylphosphine complexes of platinum(0),⁸ and therefore by using the excited state as reductant we have modified the reaction chemistry to that expected of the metal center in a lower formal oxidation state.

Mechanistically aryl halide addition occurs by a double activation induced by single electron transfer (DAISET) pathway.⁹ This $\text{S}_{\text{RN}}1$ -type mechanism first yields the odd-electron intermediates $\text{Pt}_2(\mu\text{-P}_2\text{O}_5\text{H}_2)_4^{3-}$ (d_{z^2})²(d_{z^2} *) and $\text{ArX}^{\cdot-}$ (eq 1). The



radical anion then rapidly dissociates to Ar^{\cdot} and $\text{X}^{\cdot-}$. The "cation radical" $\text{Pt}_2(\mu\text{-P}_2\text{O}_5\text{H}_2)_4^{3-}$ can then either undergo initial halide ion X^- or aryl radical Ar^{\cdot} attack to give the product $\text{Pt}_2(\mu\text{-P}_2\text{O}_5\text{H}_2)_4\text{ArX}^{4-}$. Alternatively a chain mechanism can also be initiated by the initial electron transfer step. Addition of sulfur dioxide, hydroquinone, or acrylonitrile causes the emission at 514 nm to be quenched, and no reaction with aryl halides is observed. Addition of excess bromide ion to the photochemical reaction results in the formation of $\text{Pt}_2(\mu\text{-P}_2\text{O}_5\text{H}_2)_4\text{Br}_2^{4-}$ as the sole product. This product arises from the competitive trapping of bromide ion by $\text{Pt}_2(\mu\text{-P}_2\text{O}_5\text{H}_2)_4^{3-}$, followed by the rapid disproportionation of the mixed-valence intermediate $\text{Pt}_2(\mu\text{-P}_2\text{O}_5\text{H}_2)_4\text{Br}^{4-}$.¹⁰ Addition

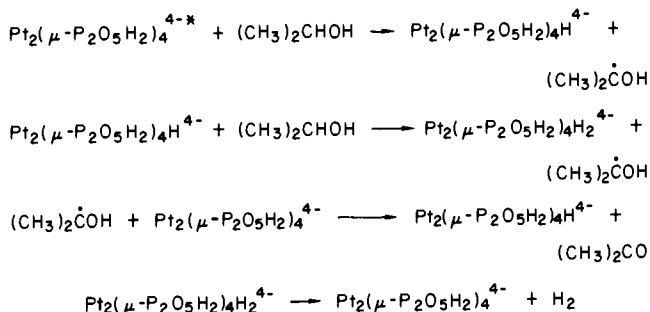
(7) The photochemical apparatus uses an Illumination Industries 200-W mercury lamp in a fan-cooled Ealing Corp. housing. Wavelength selection is made with a Schott (WG 335) sharp cutoff filter. The potassium salt of the complex is used in all reactions. Characterization data for $\text{Pt}_2(\mu\text{-P}_2\text{O}_5\text{H}_2)_4\text{ArX}^{4-}$: UV-vis λ_{max} 326 (Ar = Ph, *p*- FC_6H_4 ; X = Br), 360 (Ar = Ph; X = I), 321 (Ar = *p*- HOC_6H_4 ; X = Br) 327 (Ar = *p*- MeOC_6H_4 ; X = Br), 315 nm (Ar = Ph, X = Cl); IR (mull spectra of Pb^{2+} salts) $\nu(\text{Ph}) + \nu(\text{POP})$ 722, $\nu(\text{PO})$ 1030, 960 (Ar = Ph; X = Br), $\nu(\text{POP})$ 720, $\nu(\text{Ph})$ 825 $\nu(\text{CF})$ 1230, $\nu(\text{PO})$ 1040, 960 (Ar = *p*- FC_6H_4 ; X = Br), $\nu(\text{POP})$ 725, $\nu(\text{Ph})$ 835, $\nu(\text{PO})$ 1050, 970, $\delta(\text{OH})$ 1600, $\nu(\text{OH})$ = 3460 (Ar = *p*- HOC_6H_4 ; X = Br), $\nu(\text{POP})$ 720, $\nu(\text{Ph})$ 820, $\nu(\text{PO})$ 1040, 960 cm^{-1} (Ar = *p*- MeOC_6H_4 ; X = Br), ³¹P NMR (D_2O solutions, downfield ppm positive to H_3PO_4) δP 37.0 ($^1\text{J}(\text{PtP})$ = 2474 Hz), δP_2 32.6 ($^1\text{J}(\text{PtP})$ = 2284 Hz) (Ar = Ph; X = Br), δP_1 36.2 ($^1\text{J}(\text{PtP})$ = 2432 Hz), δP_2 31.9 ($^1\text{J}(\text{PtP})$ = 2233 Hz) (Ar = *p*- FC_6H_4 ; X = Br), δP_1 31.6 ($^1\text{J}(\text{PtP})$ = 2236 Hz), δP_2 30.5 ($^1\text{J}(\text{PtP})$ = 2428 Hz) (Ar = Ph; X = I), δP_1 36.8 ($^1\text{J}(\text{PtP})$ = 2468 Hz), δP_2 31.9 ($^1\text{J}(\text{PtP})$ = 2233 Hz) (Ar = *p*- HOC_6H_4 ; X = Br), δP_1 36.7 ($^1\text{J}(\text{PtP})$ = 2441 Hz), δP_2 32.1 ($^1\text{J}(\text{PtP})$ = 2222 Hz) (Ar = *p*- MeOC_6H_4 ; X = Br).

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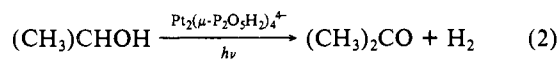
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Scheme II



of 2-methyl-2-nitrosopropane (NtB) to a photolyzed mixture of $\text{Pt}_2(\mu\text{-P}_2\text{O}_5\text{H}_2)_4^{4-}$ also causes $\text{Pt}_2(\mu\text{-P}_2\text{O}_5\text{H}_2)_4\text{Br}_2^{4-}$ to be formed instead of $\text{Pt}_2(\mu\text{-P}_2\text{O}_5\text{H}_2)_4\text{ArBr}^{4-}$.¹¹

Addition of isopropyl alcohol to the reaction as a hydrogen atom donor molecule results in hydrogen evolution and inhibition of $\text{Pt}_2(\mu\text{-P}_2\text{O}_5\text{H}_2)_4\text{ArX}^{4-}$ formation. These dehydrogenation reactions require no added aryl halide, verifying that isopropyl alcohol reacts directly with the excited state $\text{Pt}_2(\mu\text{-P}_2\text{O}_5\text{H}_2)_4^{4-*}$. Removal of the light source from the reaction causes gas evolution to cease, which shows that the conversion is photoinduced rather than photocatalyzed.¹² This reaction (eq 2) is catalytic in $\text{Pt}_2(\mu\text{-P}_2\text{O}_5\text{H}_2)_4^{4-}$ to give hydrogen and acetone.¹³ On the basis of the molar ratio of acetone formed in the reaction to $\text{Pt}_2(\mu\text{-P}_2\text{O}_5\text{H}_2)_4^{4-}$ used as catalyst, we find a turnover number exceeding 400 at a rate of 1.75 M^{-1} over a 3-h time period.



Using Gray's molecular orbital model,² the electronic configuration (d_{z^2})¹(p_z)¹ for $\text{Pt}_2(\mu\text{-P}_2\text{O}_5\text{H}_2)_4^{4-*}$ with an unpaired electron in an antibonding orbital along the Pt-Pt (z) axis can be considered to have diradical character. We propose that in the first step the secondary methine hydrogen of isopropyl alcohol is abstracted by this diradical and that this is followed by propagation steps leading to $\text{Pt}_2(\mu\text{-P}_2\text{O}_5\text{H}_2)_4\text{H}_2^{4-}$ and $(\text{CH}_3)_2\dot{\text{C}}\text{O}$ (Scheme II). Reductive elimination of H_2 from $\text{Pt}_2(\mu\text{-P}_2\text{O}_5\text{H}_2)_4\text{H}_2^{4-}$ then completes the catalytic cycle. This final reductive elimination step may be photoinduced, or like platinum(IV) dihydrides the complex $\text{Pt}_2(\mu\text{-P}_2\text{O}_5\text{H}_2)_4\text{H}_2^{4-}$ may be redox unstable.¹⁴ Microscopic reversibility arguments suggest that hydrogen elimination from dihydrides will usually follow a concerted pathway, but this is obviously impossible in this case. Apparently the reaction pathway involves initial hydrogen atom loss with H_2 being formed in a stepwise mechanism.

Isopropyl alcohol is not a unique substrate for dehydrogenation. Hydrogen evolution occurs from cyclohexanol, and small quantities of the gas are also formed from ethanol and methanol.¹⁵

(11) The EPR spectrum of the organic layer shows only the spectrum for di-tert-butyl nitroxide (see: Mackor, A.; Wajer, Th. A. J. W.; deBoer, Th. J.; van Voorst, J. D. W. *Tetrahedron Lett.* **1966**, 2115-2123). This radical is formed from the photolysis of NtB much faster than is the rate of addition of ArBr to $\text{Pt}_2(\mu\text{-P}_2\text{O}_5\text{H}_2)_4^{4-}$.

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(13) Hydrogen is detected both by addition to $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ (see, for $\nu(\text{IrH})$ and $\nu(\text{CO})$ of adduct: Vaska, L.; Diluzio, J. W. *J. Am. Chem. Soc.* **1962**, *84*, 679-680) and by GLC using a 10-ft molecular sieve 5-Å column (60-80 mesh). Acetone is detected both by ¹H NMR (δ 2.17 compared to δ 1.20 for isopropyl alcohol) and by GLC using a 10-ft silicone fluid (10%) column. Other examples of catalyzed photodehydrogenation of isopropyl alcohol: Griggs, C. G.; Smith, D. J. H. *J. Organomet. Chem.* **1984**, *273*, 105-109. Moriyama, H.; Aoki, S.; Shinoda, S.; Saito, Y. *J. Chem. Soc., Perkin Trans. 2* **1982**, 369-374. Delgado-Lieta, E.; Luke, M. A.; Jones, R. F.; Cole-Hamilton, D. J. *Polyhedron* **1982**, *1*, 839-840. Arakawa, H.; Sugi, Y. *Chem. Lett.* **1981**, 1323-1326. Irie, R.; Li, X.; Saito, Y. *J. Mol. Catal.* **1984**, *23*, 17-22, 23-27.

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Acknowledgment. We thank Professors R. D. Archer and H. Hennig for a preprint of ref 12.

Registry No. Pt₂(μ-P₂O₅H₂)₄⁴⁺, 80011-25-2; Br⁻, 24959-67-9; (C-H₃)₂CHOH, 67-63-0; H₂, 1333-74-0; PhBr, 108-86-1; *p*-FC₆H₄Br, 460-00-4; PhI, 591-50-4; *p*-HOC₆H₄Br, 106-41-2; *p*-MeOC₆H₄Br, 104-92-7; PhCl, 108-90-7; 2-methyl-2-nitrosopropane, 917-95-3.

(15) Related dehydrogenations of secondary alcohols are known where the presence of hydrogen acceptor molecules makes the reaction thermodynamically favorable; see: Djerassi, C. *Org. React.* **1951**, *6*, 207-272. Horner, L.; Kaps, U. B. *Justus Liebigs Ann. Chem.* **1980**, 192-211. Posner, G. H. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 487-296. Visintin, M.; Spogliarich, R.; Kaspar, J.; Graziani, M. *J. Mol. Catal.* **1984**, *24*, 277-280. Farnetti, E.; Vinzi, F.; Mestroni, G. *J. Mol. Catal.* **1984**, *13*, 147-164. Beaupere, D.; Nadjo, L.; Uzan, R.; Bauer, P. *J. Mol. Catal.* **1983**, *20*, 195-202.

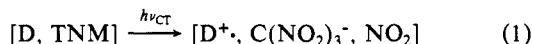
Dynamics of Transient Ion Pairs and Radical Pairs. Solvent and Salt Effects by Time-Resolved Spectroscopy

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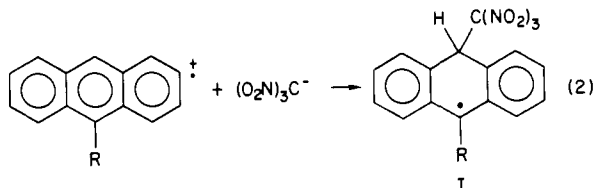
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Mechanistic studies of solvolysis reactions, pioneered by Winstein and co-workers, have heretofore provided most of the basic information relating to solvent and salt effects on reactive ion pairs.¹ We wish to show how time-resolved spectral changes can be used to examine these phenomena directly by exploiting the charge-transfer (CT) excitation of electron donor-acceptor (EDA) complexes. We previously showed that EDA complexes of various anthracene donors (D) with either tetracyanoethylene (TCNE)² or tetranitromethane (TNM)³ as the acceptor (A) produce geminate radical ion pairs [D^{•+}·A^{•-}] within 10 ps upon specific irradiation of the charge-transfer band, in accord with the expectations of Mulliken theory.⁴ Although back electron transfer is efficient in the TCNE system, it is precluded with TNM owing to the dissociative nature of its electron capture.⁵ Thus CT excitation affords D^{•+} and the fragmentation products C(NO₂)₃⁻ and NO₂ directly within the solvent cage on the time scale of <10 ps,³ i.e.,



Time-resolved picosecond spectroscopy has identified two principal routes by which this ion pair disappears. The fast component leading to hydranthryl adducts I is a cage process ($k_1 \approx 10^9$ s⁻¹)



which competes with diffusion to afford longer lived ions. The spectral identity of the hydranthryl radical is confirmed in Figure 1 by comparison with an analogous species generated independently.⁶ The slower component observed on the nanosecond time scale is attributed to the combination of D^{•+} and C(NO₂)₃⁻ subsequent to diffusive separation, and it occurs with second-order

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(6) Okada, T.; Kida, K.; Mataga, N. *Chem. Phys. Lett.* **1982**, *88*, 157.

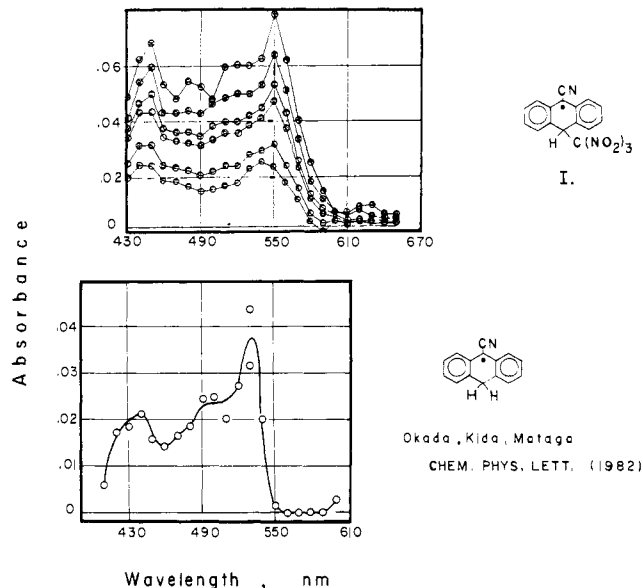


Figure 1. Upper: Typical transient absorption spectra for I disappearance at 2.0, 6.5, 14, 19, 42, and 67 μs following 532-nm excitation (1-ns fwhm pulse) of the EDA complex derived from 0.5 M 9-cyanoanthracene and 0.1 M TNM in 6:1 v/v CH₂Cl₂-CH₃OH. Lower: Transient absorption spectrum from the pulse radiolysis of 9-cyanoanthracene in ethanol containing 1% vol H₂SO₄ reproduced from ref 6 on the same wavelength scale.

Table I. Rates of Elementary Processes for Anthracene Cations^a

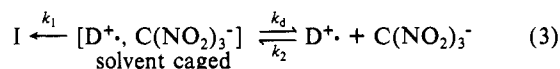
9-R-10-R'-anthracene	k_{obsd}^b M ⁻¹ /s ⁻¹	k_1^c / ($k_1 + k_d$)	k_2 , M ⁻¹ s ⁻¹	k_1 , s ⁻¹	k_2/k_d , M ⁻¹
H, H	1.6×10^{11}	0.91	1.8×10^{11}	1.5×10^9 ^d	1200
C ₆ H ₅ , H	1.5×10^{11}	0.70	2.1×10^{11}	1.3×10^9 ^e	1400 ^e
Br, H	1.7×10^{11}	0.92	1.8×10^{11}	3.3×10^9 ^e	1200 ^e
CH ₂ =CH, H	1.4×10^{11}	0.64	2.2×10^{11}	0.8×10^9 ^e	1400 ^e

^a At 25 °C in CH₂Cl₂, [D] = 0.05 M, [TNM] = 0.1 M.

^b Calculated from eq 4 by assuming $\epsilon_{\text{max}} = 7700$ M⁻¹ cm⁻¹ from ref 10.

^c Estimated from intensity calibrations by using a hematoporphyrin IX standard ($\epsilon_{440} = 14000$, $\Phi_{\text{isc}} = 0.83$).¹² ^d Calculated from picosecond spectra in ref 3; $k_d = 3.4 \times 10^8$ s⁻¹. ^e Assuming k_d is invariant with substituents.

kinetics (k_{obsd}). Proceeding from the ion-pair formulation used in solvolytic mechanisms,⁷ we represent our composite scheme as



for which the kinetics are⁸

$$-\frac{dA}{dt} = k_{\text{obsd}}[D^{\bullet+}][C(NO_2)_3^{\bullet-}] = \frac{k_1 k_2}{k_d + k_1} [D^{\bullet+}]^2 \quad (4)$$

Values of k_2 obtained from the experimental k_{obsd} and the measured fraction of cage collapse, i.e., $k_1/(k_d + k_1)$, are presented in Table I. Knowledge of $k_1 = 1.5 \times 10^9$ s⁻¹ for anthracene, which is obtained directly from the picosecond data,³ yields $k_d = 4.2 \times 10^8$ s⁻¹. It is noteworthy that the values of k_2 obtained in this manner are significantly larger than diffusional rates of neutral species.⁹ This is expected to result from the extra Coulombic

(7) See: Shiner, Jr., V. J. In "Isotopes Effects in Chemical Reactions"; Collins, C. J., Bowman, N. S., Eds.; Van Nostrand Reinhold: New York, 1970.

(8) A is the absorbance of D^{•+} at λ_{max} . The low concentrations ($\sim 10^{-5}$ M) of ions justifies the steady-state approximation.

(9) Weston, R. E., Jr.; Schwarz, H. A. "Chemical Kinetics"; Prentice Hall: Englewood Cliffs, NJ, 1972; p 151 ff. Gordon, A. J.; Ford, R. A. "The Chemist's Companion"; Wiley: New York, 1972; pp 136-137. Compare also: Ritchie, C. D.; VanVerth, J. E.; Virtanen, P. O. *J. Am. Chem. Soc.* **1982**, *104*, 3491 and related papers.