

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

**Registry No.** Pt<sub>2</sub>(μ-P<sub>2</sub>O<sub>5</sub>H<sub>2</sub>)<sub>4</sub><sup>4+</sup>, 80011-25-2; Br<sup>-</sup>, 24959-67-9; (C-H<sub>3</sub>)<sub>2</sub>CHOH, 67-63-0; H<sub>2</sub>, 1333-74-0; PhBr, 108-86-1; *p*-FC<sub>6</sub>H<sub>4</sub>Br, 460-00-4; PhI, 591-50-4; *p*-HOC<sub>6</sub>H<sub>4</sub>Br, 106-41-2; *p*-MeOC<sub>6</sub>H<sub>4</sub>Br, 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.

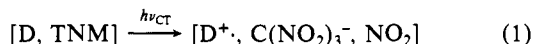
## Dynamics of Transient Ion Pairs and Radical Pairs. Solvent and Salt Effects by Time-Resolved Spectroscopy

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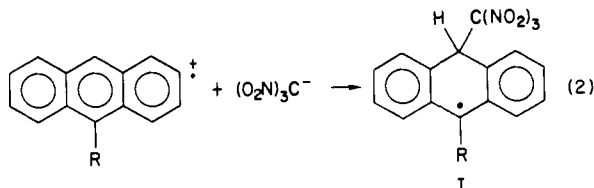
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Received January 21, 1985

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.<sup>1</sup> 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)<sup>2</sup> or tetranitromethane (TNM)<sup>3</sup> as the acceptor (A) produce geminate radical ion pairs [D<sup>•+</sup>A<sup>-</sup>] within 10 ps upon specific irradiation of the charge-transfer band, in accord with the expectations of Mulliken theory.<sup>4</sup> Although back electron transfer is efficient in the TCNE system, it is precluded with TNM owing to the dissociative nature of its electron capture.<sup>5</sup> Thus CT excitation affords D<sup>•+</sup> and the fragmentation products C(N-O<sub>2</sub>)<sub>3</sub><sup>-</sup> and NO<sub>2</sub> directly within the solvent cage on the time scale of <10 ps,<sup>3</sup> 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<sup>-1</sup>)



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.<sup>6</sup> The slower component observed on the nanosecond time scale is attributed to the combination of D<sup>•+</sup> and C(N-O<sub>2</sub>)<sub>3</sub><sup>-</sup> subsequent to diffusive separation, and it occurs with second-order

(1) Winstein, S.; Robinson, G. C. *J. Am. Chem. Soc.* **1958**, *80*, 169. Harris, J. M. *Prog. Phys. Org. Chem.* **1974**, *11*, 89.

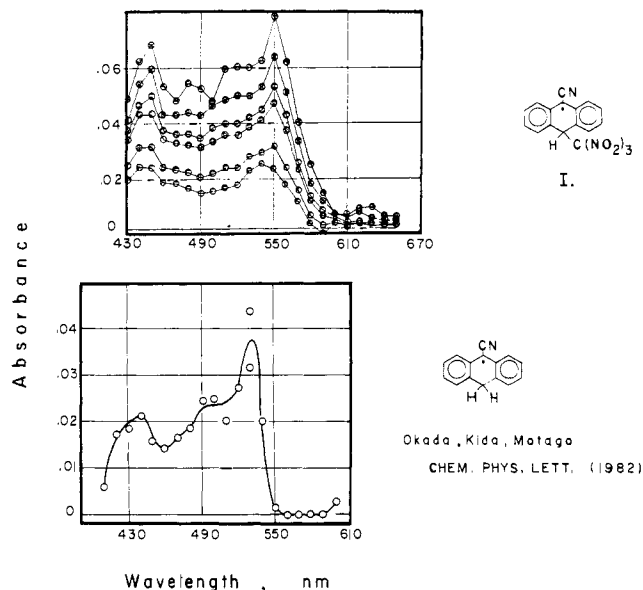
(2) Hilinski, E. F.; Masnovi, J. M.; Amatore, C.; Kochi, J. K.; Rentzepis, P. M. *J. Am. Chem. Soc.* **1983**, *105*, 6167; **1984**, *106*, 8071.

(3) Masnovi, J. M.; Huffman, J. C.; Kochi, J. K.; Hilinski, E. F.; Rentzepis, P. M. *Chem. Phys. Lett.* **1984**, *106*, 20.

(4) Mulliken, R. S. *J. Am. Chem. Soc.* **1952**, *74*, 811. Mulliken, R. S., Person, W. B. "Molecular Complexes: A Lecture and Reprint Volume"; Wiley: New York, 1969.

(5) Chaudhuri, S. A.; Asmus, K. D. *J. Phys. Chem.* **1972**, *76*, 26.

(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 CH<sub>2</sub>Cl<sub>2</sub>-CH<sub>3</sub>OH. Lower: Transient absorption spectrum from the pulse radiolysis of 9-cyanoanthracene in ethanol containing 1% vol H<sub>2</sub>SO<sub>4</sub> reproduced from ref 6 on the same wavelength scale.

**Table I.** Rates of Elementary Processes for Anthracene Cations<sup>a</sup>

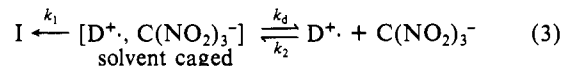
9-R-10-R'-anthracene	$k_{obsd}^b$ M <sup>-1</sup> /s <sup>-1</sup>	$k_1^c/-$ ( $k_1 + k_d$ )	$k_2$ , M <sup>-1</sup> s <sup>-1</sup>	$k_1$ , s <sup>-1</sup>	$k_2/k_d$ , M <sup>-1</sup>
H, H	$1.6 \times 10^{11}$	0.91	$1.8 \times 10^{11}$	$1.5 \times 10^9$ <sup>d</sup>	1200
C <sub>6</sub> H <sub>5</sub>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

<sup>a</sup> At 25 °C in CH<sub>2</sub>Cl<sub>2</sub>, [D] = 0.05 M, [TNM] = 0.1 M.

<sup>b</sup> Calculated from eq 4 by assuming  $\epsilon_{max}$  7700 M<sup>-1</sup> cm<sup>-1</sup> from ref 10.

<sup>c</sup> Estimated from intensity calibrations by using a hematoporphyrin IX standard ( $\epsilon_{440}$  14 000,  $\Phi_{isc}$  0.83).<sup>12</sup> <sup>d</sup> Calculated from picosecond spectra in ref 3;  $k_d$  =  $3.4 \times 10^8$  s<sup>-1</sup>. <sup>e</sup> Assuming  $k_d$  is invariant with substituents.

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



for which the kinetics are<sup>8</sup>

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

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<sup>-1</sup> for anthracene, which is obtained directly from the picosecond data,<sup>3</sup> yields  $k_d = 4.2 \times 10^8$  s<sup>-1</sup>. It is noteworthy that the values of  $k_2$  obtained in this manner are significantly larger than diffusional rates of neutral species.<sup>9</sup> 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<sup>•+</sup> at  $\lambda_{max}$ . 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.

**Table II.** Second-Order Rate Constants for the Disappearance of Anthracene Cations ( $D^+$ ) Derived from the CT Excitation of Anthracene-TNM Complexes

9-R-10-R'-anthracene	$\lambda_{\max}(D^+)$ , nm <sup>a</sup>	$\log k_{\text{obsd}}, A^{-1} s^{-1}$					
		$CH_2Cl_2$ <sup>b</sup>	$F^c$	TBAP <sup>b,d</sup>	$F^c$	$CH_3CN$ <sup>e</sup>	$F^c$
CHO, H	735	<i>f</i>	0.05	<i>g</i>		5.6	0.3
H, H	710 <sup>h</sup>	7.62	0.09	5.4	0.7	5.6	0.7
C <sub>6</sub> H <sub>5</sub> , H	720	7.59	0.3	5.5	0.8	5.7	0.7
Br, H	725	7.64	0.08	5.5	0.7	5.5	0.7
CH <sub>2</sub> =CH, H	690	7.57	0.4	5.5	0.8	5.3	0.6
CHO, Cl	750	<i>f</i>	0.04	<i>g</i>		5.4	~1
CHO, CH <sub>3</sub>	720	7.6	0.07	5.1	0.14	5.1	0.23
Br, Br	710	5.9 <sup>i</sup>	~1	<5 <sup>i</sup>	~1	5.1 <sup>i</sup>	~1
C <sub>6</sub> H <sub>5</sub> , C <sub>6</sub> H <sub>5</sub>	660	4.1	~1	4.1	~1	4.1	~1
CH <sub>3</sub> , CH <sub>3</sub>	650	5.4	~1	5.3	~1	5.4	~1
NO <sub>2</sub> , H	760	<i>f</i>	0.03	<i>g</i>		<i>j</i>	0.1
CN, H	770	<i>f</i>	0.02	<i>j</i>	0.15	<i>g</i>	
CH <sub>3</sub> O, H	610	6.3	~1	6.0	~1	<i>g</i>	

<sup>a</sup>Monitoring wavelength. <sup>b</sup>[TNM] = 0.1 M, [D] = 0.05 M. <sup>c</sup> $F = k_d/(k_1 + k_d)$  estimated from intensity calibrations. <sup>d</sup>0.1 M tetra-*n*-butylammonium perchlorate in  $CH_2Cl_2$ . <sup>e</sup>[TNM] ~ 0.2 M, [D] saturated (~0.01–0.02 M). <sup>f</sup>Insufficient signal. <sup>g</sup>Not determined. <sup>h</sup> $\epsilon_{\max} = 7700 M^{-1} cm^{-1}$ , in ref 10. <sup>i</sup>Decay appears to contain appreciable first-order components. <sup>j</sup>Complex decay kinetics.

**Table III.** Second-Order Rate Constants ( $k_3$  in eq 5) for the Disappearance of Hydranthryl Radicals I Derived from Eq 2<sup>a</sup>

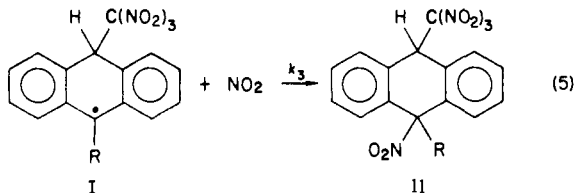
9-R-10-R'-anthracene	$\lambda_{\max}(I)$ , nm	$\log k_3, A^{-1} s^{-1}$		
		$CH_2Cl_2$	$CH_2Cl_2$ (TBAP)	$CH_3CN$
NO <sub>2</sub> , H	550 <sup>b</sup>	5.5	5.9	5.6
CN, H	545	5.8	5.8	5.8
CHO, H	545	5.7	6.1	5.7
CHO, CH <sub>3</sub>	560	6.1	<i>c</i>	<i>c</i>

<sup>a</sup>Under the conditions given in Table II. <sup>b</sup> $\epsilon_{\max} 1300 M^{-1} cm^{-1}$ , assuming  $\epsilon_{\max} 7700 M^{-1} cm^{-1}$  for  $D^+$  (see ref 10). <sup>c</sup>Overlaps radical cation absorptions.

attraction, which we believe to be also responsible for the stability of the ion pair, as indicated in the last column in Table I.

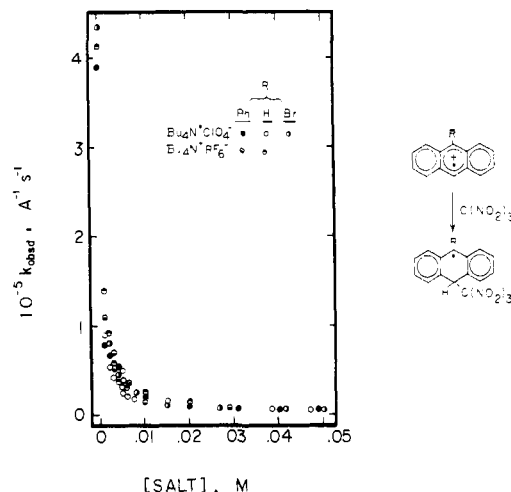
Three factors influence the rate of the disappearance of ions—namely, the substituents on D, the solvent polarity, and added salts as listed in the top of Table II. Thus electron-releasing substituents ( $R = CH_3O, C_6H_5$ ) stabilize  $D^+$  and decrease its rate of annihilation. This is also reflected in the increased fraction of ions that survive cage collapse (compare the values in parentheses). At the other extreme,  $D^+$  with electron-attracting substituents ( $NO_2, CN$ ) is more reactive and does not escape cage collapse, as shown by the absence of these ion absorptions on the nanosecond time scale. Next, the kinetics of ion disappearance are at least two orders of magnitude faster in dichloromethane solution than in the more polar acetonitrile. Note that  $CH_3CN$  exerts a marked leveling effect on the rates of ion disappearance. Finally, the presence of innocent salts such as  $Bu_4N^+ClO_4^-$  leads to the same diminution and leveling effect on the rates of ion disappearance in  $CH_2Cl_2$  even at low concentrations (see Figure 2). The common ion effect in this system can be observed by the addition of  $Bu_4N^+C(NO_2)_3^-$ , whereupon the ion disappearance follows first-order kinetics.

Time-resolved spectroscopy allows us to also examine the dynamics of radical-radical interactions. Thus the series of spectra in Figure 1, top, typically illustrate the decay of the hydranthryl radical with  $NO_2$  to form the meso adduct II, which we have



isolated in high yields ( $\Phi \sim 1$ ). Analysis of these data indicates that I disappears with second-order kinetics (see Table III). The rate constant  $k_3$  for this radical association is singularly unaffected

(10) Torikai, A.; Kato, R. *J. Polym. Sci., Polym. Chem. Ed.* **1978**, *16*, 1487.



**Figure 2.** Effect of innocent salts (tetra-*n*-butylammonium perchlorate and hexafluorophosphate) on the observed rate of decay ( $k_{\text{obsd}}$ ) of various anthracene cations in  $CH_2Cl_2$  as in Table II.

by either the substituent on anthracene, the solvent polarity, or the presence of salt. Thus ions and radicals show strongly contrasting behavior, as underscored by the solvent and salt effects presented in Table II. The basic difference arises from the mutual annihilation of charge in cation-anion pairs which is absent in radical-radical interactions. Broadly speaking, the ionic process is the microscopic reverse of the classical  $S_N1$  mechanism. As such, the CT generation and time-resolved observation of ion pairs will provide direct access to the dynamics of ion behavior in solution,<sup>11</sup> critical to solvolytic mechanisms.

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**Registry No.** I(9- $NO_2$ ,10-H), 96705-32-7; I(9-CN,10-H), 96705-33-8; I(9-CHO,10-H), 96705-34-9; I(9-CHO,10-Me), 96705-35-0; D(9-CH-

(11) See, for solvent and salt effects on the related case of exciplex quenching: Weller, A. *Pure Appl. Chem.* **1968**, *16*, 115. Hino, T.; Akazawa, H.; Masuhara, H.; Mataga, N. *J. Phys. Chem.* **1976**, *80*, 33. Simon, J. D.; Peters, K. S. *Acc. Chem. Res.* **1984**, *17*, 277. Goodson, B. E.; Schuster, G. B. *J. Am. Chem. Soc.* **1984**, *106*, 7254. For a review: Gordon, M.; Ware, W. R. "The Exciplex"; Academic Press: New York, 1975. See also, for a comparison: Mataga, N. *Pure Appl. Chem.* **1984**, *56*, 1255.

(12) Reddi, E.; Jori, G.; Rodgers, M. A. J.; Spikes, J. D. *Photochem. Photobiol.* **1983**, *38*, 639.

O,10-H)-C(NO<sub>2</sub>)<sub>4</sub>, 91452-22-1; D<sup>+</sup>-(9-CHO,10-H), 91547-89-6; D(9-H,10-H)-C(NO<sub>2</sub>)<sub>4</sub>, 36301-08-3; D<sup>+</sup>-(9-H,10-H), 34512-28-2; D(9-Ph,10-H)-C(NO<sub>2</sub>)<sub>4</sub>, 91452-18-5; D<sup>+</sup>-(9-Ph,10-H), 40807-34-9; D(9-Br,10-H)-C(NO<sub>2</sub>)<sub>4</sub>, 91452-19-6; D<sup>+</sup>-(9-Br,10-H), 84985-63-7; D(9-C<sub>6</sub>H<sub>5</sub>-CH=CH,10-H)-C(NO<sub>2</sub>)<sub>4</sub>, 96689-10-0; D<sup>+</sup>-(9-CH<sub>2</sub>=CH,10-H), 96689-17-7; D(9-CHO,10-Cl)-C(NO<sub>2</sub>)<sub>4</sub>, 96689-11-1; D<sup>+</sup>-(9-CHO,10-Cl), 93350-37-9; D(9-CHO,10-Me)-C(NO<sub>2</sub>)<sub>4</sub>, 96689-12-2; D<sup>+</sup>-(9-CHO,10-Me), 96689-18-8; D(9-Br,10-Br)-C(NO<sub>2</sub>)<sub>4</sub>, 96689-13-3; D<sup>+</sup>-(9-Br,10-Br), 51939-74-3; D(9-Ph,10-Ph)-C(NO<sub>2</sub>)<sub>4</sub>, 96689-14-4; D<sup>+</sup>-(9-Ph,10-Ph), 34480-04-1; D(9-Me,10-Me)-C(NO<sub>2</sub>)<sub>4</sub>, 96689-15-5; D<sup>+</sup>-(9-Me,10-Me), 34526-95-9; D(9-NO<sub>2</sub>,10-H)-C(NO<sub>2</sub>)<sub>4</sub>, 91452-21-0; D<sup>+</sup>-(9-NO<sub>2</sub>,10-H), 84367-93-1; D(9-CN,10-H)-C(NO<sub>2</sub>)<sub>4</sub>, 91452-20-9; D<sup>+</sup>-(9-CN,10-H), 84985-64-8; D(9-OMe,10-H)-C(NO<sub>2</sub>)<sub>4</sub>, 96689-16-6; D<sup>+</sup>-(9-OMe,10-H), 84367-94-2; C(NO<sub>2</sub>)<sub>3</sub><sup>-</sup>, 20143-63-9; NO<sub>2</sub><sup>-</sup>, 10102-44-0.

## Inter- and Intramolecular Oxidative Addition of Phosphine, Methane, Alkane, and Alkene C-H Bonds to Rhenium

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Intermolecular oxidative addition of C-H bonds in alkanes to soluble transition-metal complexes, leading to stable hydrido(alkyl)metal complexes (eq 1), has so far been observed only with

$$M + R-H \rightarrow R-M-H \quad (1)$$

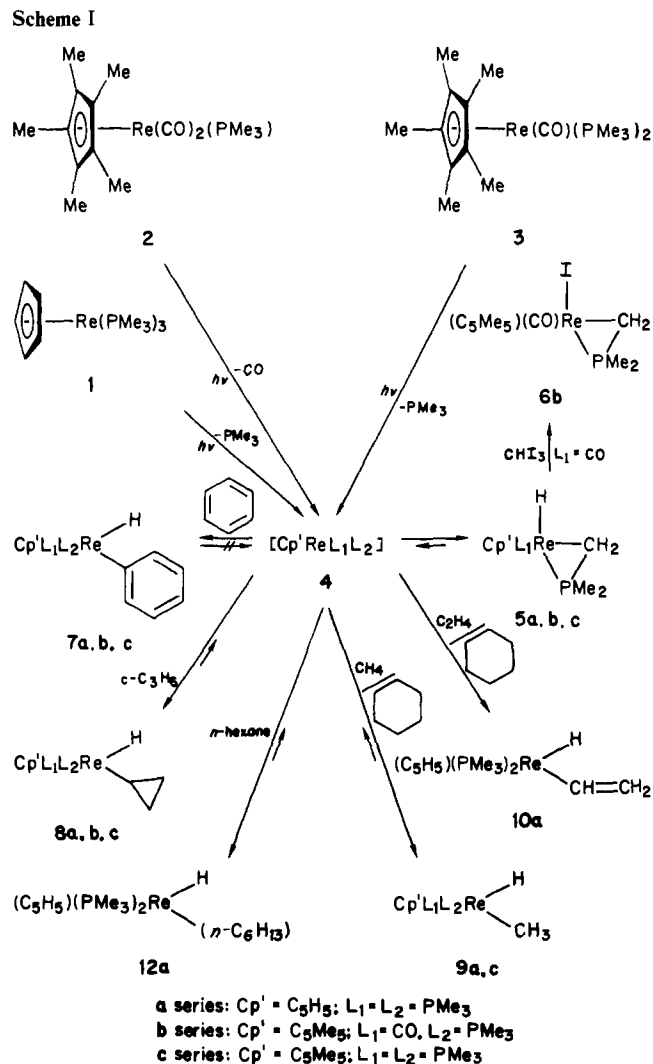
iridium and rhodium complexes.<sup>1</sup> We now wish to report the first direct observation of this reaction at rhenium. These new C-H activation reactions exhibit the following behavior which contrasts with that observed in the earlier-studied systems: (1) Competitive intermolecular alkane C-H activation and intramolecular attack on C-H bonds in PMe<sub>3</sub> ligands is observed. (2) The cyclometalated products provide a route to thermal activation of hydrocarbons under mild conditions. (3) Despite lowered inter/intra selectivity, selectivity with respect to different alkanes is substantially increased. Primary, cyclopropyl, methane, aromatic, and vinyl hydrogens are attacked, but secondary and tertiary C-H bonds are not. Thus cyclohexane can be used as an inert solvent, providing a convenient method for activating gaseous substrates such as methane and ethylene. (4) The efficiency of oxidative addition depends markedly upon the ligands attached to the metal.

Our observations are summarized in Scheme I. Analogous, although not identical, results have been obtained in three systems for which CpRe(PMe<sub>3</sub>)<sub>2</sub> (**4a**), (C<sub>5</sub>Me<sub>5</sub>)Re(CO)(PMe<sub>3</sub>) (**4b**), and (C<sub>5</sub>Me<sub>5</sub>)Re(PMe<sub>3</sub>)<sub>2</sub> (**4c**) are postulated as intermediates. These reactive species are accessible via the new photochemical precursors **1**, **2**, and **3** and/or thermally from the cyclometalated complexes (vide infra) **5**. Carbonyl(phosphine) complexes **2** and **3** are prepared (41% and 22% isolated yield, respectively) in straightforward photosubstitution reactions involving (C<sub>5</sub>Me<sub>5</sub>)Re(CO)<sub>3</sub> and PMe<sub>3</sub>. Complex **1** was formed in 35% yield by reduction of ReCl<sub>3</sub>(PMe<sub>3</sub>)<sub>3</sub><sup>3</sup> in the presence of cyclopentadiene; a similar synthesis of the analogous C<sub>5</sub>Me<sub>5</sub> complex by this route could not be accomplished.

(1) (a) Janowicz, A. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1982**, *104*, 352; *Ibid.* **1983**, *105*, 3929. (b) Hoyano, J. K.; Graham, W. A. G. *Ibid.* **1982**, *104*, 3723. (c) Bergman, R. G. *Science (Washington, D.C.)* **1984**, *223*, 902. (d) Jones, W. D.; Feher, F. J. *Organometallics* **1983**, *2*, 562; *J. Am. Chem. Soc.* **1984**, *106*, 1650. (e) Periana, R. A.; Bergman, R. G. *Organometallics* **1984**, *3*, 508; *J. Am. Chem. Soc.* **1984**, *106*, 7272.

(2) For an interesting dinuclear relative of this complex, see: Chiu, K. W.; Howard, C. G.; Rzepa, H. S.; Sheppard, R. N.; Wilkinson, G.; Galas, A. M. R.; Hursthouse, M. B. *Polyhedron* **1982**, *1*, 441.

(3) The preparation of this material involved modification of procedures worked out earlier for related (phosphine)rhenium complexes; cf.: Douglas, P. G.; Shaw, B. L. *Inorg. Synth.* **1977**, *17*, 64.



Our cleanest results overall have been obtained on photolysis of the cyclopentadienyltris(phosphine) complex **1**. For example, photolysis<sup>4</sup> of **1** in benzene or cyclopropane leads to the corresponding products of C-H oxidative addition **7a** and **8a**.<sup>5</sup> These materials can be isolated in good yields (64% and 21%, respectively) by recrystallization (**7a**) or by air-free chromatography at -100 °C on alumina III (**8a**) and were characterized fully by spectroscopic and conventional analytical methods. Irradiation of **1** in *n*-hexane at -30 °C produces a C-H activation product identifiable by <sup>1</sup>H NMR (hydride resonance appears as t of t, <sup>3</sup>J<sub>H-H</sub> = 3.6, <sup>2</sup>J<sub>H-P</sub> = 50.1 Hz) as the primary C-H insertion product **12a** (38% NMR yield after 72% conversion).<sup>6</sup> Most of these C-H activation products are stable for significant lengths of time (e.g., several hours) at 25 °C. Hydrido *n*-hexyl complex **12a** is significantly less stable, reductively eliminating *n*-hexane at 20 °C with a half-life of ca. 12 min. We have not yet succeeded in isolating this material in pure form. In contrast to earlier observations in the iridium and rhodium series, irradiation of **1** in cyclohexane does *not* lead to intermolecular C-H insertion.

(4) Photolyses were performed in Pyrex vessels using a 450-W medium-pressure Hanovia lamp at ca. 5 °C unless otherwise noted. A 100-W medium-pressure Hanovia lamp was used in the synthesis of compounds **3**, **5b**, and **5c**.

(5) On the basis of NMR spectra we assign the stereochemistry of the oxidative addition products as *trans*, although we cannot rule out rapidly equilibrating geometries. The stereochemistry of the cyclometalated products **5** has not yet been assigned.

(6) Small amounts (<5%) of Cp'ReL<sub>2</sub>H<sub>2</sub> (Cp' = C<sub>5</sub>H<sub>5</sub>, C<sub>5</sub>Me<sub>5</sub>; L = PMe<sub>3</sub>) are observed in many of the photolyses. Prolonged photolysis results in somewhat higher yields of the dihydride, along with concurrent destruction of the C-H oxidative addition product. The related complex CpRe(PPh<sub>3</sub>)<sub>2</sub>H<sub>2</sub> is known: Baudry, D. H.; Ephretikhine, M. *J. Chem. Soc., Chem. Commun.* **1980**, 249.