

Table I. Aromatic Hydrocarbon Singlet Quenching Rate Constants

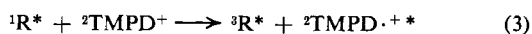
	Fluoranthene (358) ^a	Chrysene (316)	1,2-Benzanthracene (358)	Pyrene (357)	Naphthalene (316)
τ_F^0 (nsec)	52.6	48.1	46.1	323.6	107.2
$\Delta E_{S_1-T_1}$ (cm ⁻¹) ^b	6800 ^c	7700	9500	10,100	10,500
$-E_{1/2}(R/R\cdot^-)$ ^d	1.81 ^e	2.25	2.00	2.07	2.47
$E_{1/2}(R/R\cdot^+)$ ^d	1.45	1.35	1.18	1.26	1.54
$k_q(^2\text{TMPD}\cdot^+) \times 10^{-10}$ (M ⁻¹ sec ⁻¹) ^f	2.60 ± 0.06 ^g	2.10 ± 0.15	2.11 ± 0.15	2.15 ± 0.05	3.0 ± 0.30
$k_q(\text{TMPD}) \times 10^{-10}$ (M ⁻¹ sec ⁻¹)	1.99 ± 0.05		1.47 ^h		
$k_q(\text{DTBN}) \times 10^{-10}$ (M ⁻¹ sec ⁻¹) ⁱ		0.85	0.80	0.78 1.14 ^j	0.82

^a Numbers in parentheses are wavelengths of excitation in nm. ^b C. S. Parmenter and J. D. Rau, *J. Chem. Phys.*, **51**, 2242 (1969). ^c Taken from J. B. Briks, "Photophysics of Aromatic Molecules," Wiley, New York, N. Y., 1970, pp 75 and 261. ^d Taken from C. K. Mann and K. K. Barnes, "Electrochemical Reaction in Nonaqueous Media," Marcel Dekker, New York, N. Y., 1970; in volts vs. sce. ^e K. F. Drake, unpublished results, Northwestern University, 1972. ^f In 0.1 M TBAP-CH₃CN solutions. ^g Standard deviation for least-squares fit to eq 2. ^h Reference 10. ⁱ Reference 3, in methylcyclohexane. ^j Reference 3, in acetonitrile.

aromatic hydrocarbon self-interactions were observed in the fluorescence spectra.

The results of fluorescence lifetime quenching studies on five aromatic hydrocarbon-²TMPD⁺ systems are presented in Table I. One can calculate an upper limit to the diffusion controlled rate constant, k_{diff} , for a bimolecular quenching process from the Smoluchowski relation¹⁰ equal to $2.4 \times 10^{10} \text{ M}^{-1} \text{ sec}^{-1}$. The results in Table I show that ²TMPD⁺ is an effective singlet quencher with a quenching rate constant near to or somewhat greater than k_{diff} . Also included in Table I for comparison purposes are quenching rate constants for systems involving TMPD and DTBN as the quencher. In those cases where the available data permit a comparison, ²TMPD⁺ is seen to react *faster* than TMPD. Since the diffusion coefficient of a radical ion is either essentially equal to^{9a} or smaller than^{9b} the diffusion coefficient of the corresponding neutral, this rate difference may be attributed to a larger interaction radius for the ²TMPD⁺ quenching mechanism than the TMPD electron transfer quenching mechanism.¹⁰ In addition ²TMPD⁺ quenches pyrene fluorescence 1.9 times faster than DTBN in acetonitrile. Since this rate difference is also too large to be accounted for in terms of quencher diffusion coefficient differences, the interaction radius hypothesis may apply here also.

The data obtained in this preliminary investigation do not permit a definitive assignment of the ²TMPD⁺ fluorescence quenching mechanism; however, we can rule out processes such as



since $k_q(^2\text{TMPD}\cdot^+)$ is near k_{diff} for all five hydrocarbons even though $\Delta E_{S_1-T_1}$ is less than the energy of the lowest allowed doublet-doublet transition in ²TMPD⁺ (16,350 cm⁻¹). The lack of correlation between $k_q(^2\text{TMPD}\cdot^+)$ and either $E_{1/2}(R/R\cdot^-)$ or $E_{1/2}(R/R\cdot^+)$ argues against an electron transfer mechanism analogous to that for quenching by TMPD. Collisional energy transfer,¹¹ electron-exchange induced intersystem crossing, and vibrational quenching¹² must all be considered possible mechanisms at this time. Further examination of the $k_q(^2\text{TMPD}\cdot^+)$ values shows that

- (9) (a) R. V. Slaters and M. Szwarc, *J. Phys. Chem.*, **69**, 4124 (1965);
 (b) G. Cauquis and D. Serve, *Anal. Chem.*, **44**, 2222 (1972).
 (10) D. Rehm and A. Weller, *Isr. J. Chem.*, **8**, 259 (1970).
 (11) D. L. Dexter, *J. Chem. Phys.*, **21**, 836 (1953).
 (12) A. M. Braun, W. B. Hammond, and H. G. Cassidy, *J. Amer. Chem. Soc.*, **91**, 6196 (1969).

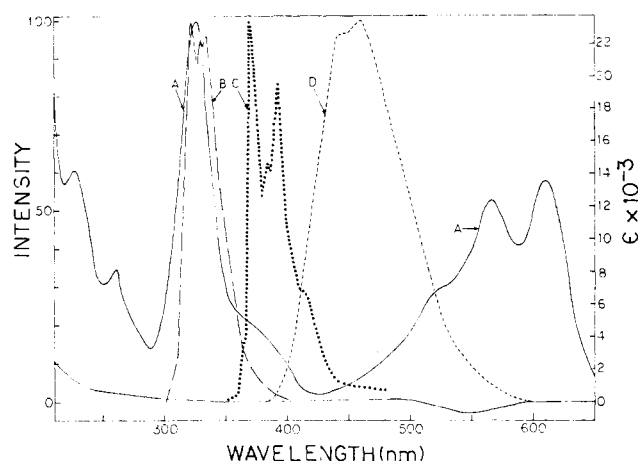


Figure 1. Spectral overlap characteristics of aromatic hydrocarbon fluorescence spectra and Wurster's blue cation radical absorption spectrum: A, Wurster's blue cation radical absorption spectrum in 0.1 M TBAP-acetonitrile solution; B, naphthalene fluorescence spectrum, 10^{-2} N in acetonitrile; C, pyrene fluorescence spectrum, 10^{-4} M in acetonitrile; D, fluoranthene fluorescence spectrum, 10^{-4} M in acetonitrile.

they fall into two groups: (i) chrysene, 1,2-benzanthracene, and pyrene with k_q near $2.1 \times 10^{10} \text{ M}^{-1} \text{ sec}^{-1}$ and (ii) fluoranthene and naphthalene with $k_q > k_{diff}$. This grouping correlates with the extent of spectral overlap between the hydrocarbon donor fluorescence transition and the strongly allowed ²TMPD⁺ acceptor absorption transitions. The spectral overlap characteristics are shown in Figure 1. The fluorescence spectra of chrysene and 1,2-benzanthracene are similar to that of pyrene and do not overlap appreciably with any ²TMPD⁺ absorption bands. A tentative interpretation of this correlation is that, in the cases of fluoranthene and naphthalene, ²TMPD⁺ quenching involves a long-range resonance energy transfer mechanism¹³ as well as a collisional energy transfer mechanism; whereas, for the other hydrocarbons the collisional mechanism is the only reactive channel available since there is virtually no spectral overlap. The resonance mechanism apparently does not predominate in either the fluoranthene or naphthalene cases since the values of k_q are only slightly greater than k_{diff} . This may be qualitatively understood on the basis that the degree of spectral overlap between ²TMPD⁺ absorption and fluoranthene emission is small and in the case of

- (13) Th. Forster, *Discuss. Faraday Soc.*, **27**, 7 (1959).

naphthalene although there is very strong spectral overlap the oscillator strength of the naphthalene transition is low.¹⁴

Acknowledgment. The assistance of Messrs. Dennis Rushforth, Charles Lombard, and Jeffrey K. McVey during various phases of this work is acknowledged. The author wishes to thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, The Research Corporation, and the National Science Foundation (GP-32953) for support of this research.

(14) I. B. Berlman, "Handbook of Fluorescence Spectra of Aromatic Molecules," Academic Press, New York, 1971, p 330.

Richard P. Van Duyne

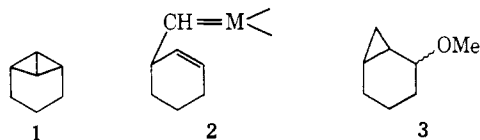
Department of Chemistry, Northwestern University
Evanston, Illinois 60201

Received June 20, 1973

Transition Metal Catalyzed Rearrangements of Bicyclobutanes. Mechanism of Acid Production in Methanolysis¹

Sir:

In our recent investigation of the transition metal catalyzed isomerization of tricyclo[4.1.0.0^{2,7}]heptane (1), the involvement of an organometallic carbene intermediate (2) was indicated.² It was also shown that the formation of 2-norcarane methyl ether (3) in the



reaction of 1 with $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ in methanol resulted from a protic acid catalyzed reaction. These methanolic studies have been extended to substituted bicyclobutanes and, again, all reaction solutions became acidic. We now present evidence as to the nature of the acid-forming species.

As in our initial studies, solid $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ was added to a methanol solution of the bicyclobutane, with and without solid NaHCO_3 . Table I lists the results of the study. When NaHCO_3 was absent, the pH³ rapidly dropped from about 8.0 for the bicyclobutane-methanol solution to about 2.5 when the Rh(I) catalyst was added, and the pH slowly increased.⁴ With NaHCO_3 present, the pH only dropped to 5.0 and then rapidly increased.⁵

(1) This work was supported by National Science Foundation Grant No. GP-8700.

(2) (a) W. G. Dauben and A. J. Kielbania, Jr., *J. Amer. Chem. Soc.*, **94**, 3669 (1972); (b) see also S. Masamune, M. Sakai, and N. Darby, *J. Chem. Soc., Chem. Commun.*, 471 (1972).

(3) We monitored the pH of reaction solutions using a Sargent-Welch Model NX digital pH meter with a Sargent-Welch combination glass electrode S300 72-15. See R. G. Bates, "Determination of pH—Theory and Practices," Wiley, New York, N. Y., 1964.

(4) (a) The addition of $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ to methanol without bicyclobutanes present results in a rapid decrease in pH from about 8.0 to 4.0. This pH drop may be due to a bridge splitting reaction by methanol resulting in a rhodium complex in which methanol has been incorporated as a ligand. (b) See D. N. Lawson and G. Wilkinson, *J. Chem. Soc.*, 1900 (1965). (c) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 3rd ed, Wiley, New York, N. Y., 1972, p 1020.

(5) It was found that when 1 was allowed to react for 2 min in methanol of pH 3.4 only 3 was detected in the reaction solution. Using methanol of pH 4.4 after 2 min both 1 (66%) and 3 (34%) were identified.

Table I. Reactions of $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ and Bicyclobutanes in Methanol

Reactant	Products and reaction conditions		
1	3 100% ^a 10%	4 0% ^a 90% ^b	
5	6 84% ^a 72% ^b	7 16% ^a 13% ^b	8 0% ^a 15% ^b
9	10 100% ^a 90% ^b	11 0% ^a 10% ^b	
12	13 75% ^a 73% ^b	14 25% ^a 25% ^b	15 0% ^a 0% ^b

^a Reactions were performed using 5 ml of methanol and a mole ratio of bicyclobutane to Rh(I) catalyst of approximately 20:1; 8 mg of Rh(I) catalyst was added to a methanolic solution of the bicyclobutane. Reaction times were approximately 10 min. Product distributions were analyzed by nmr and vpc and are normalized. In general as the degree of substitution on the bicyclobutane increased, product formation was not as quantitative as in the case of 1. ^b Same reaction conditions as in footnote a with 50 mg of sodium bicarbonate present.

Recently, Gassman and Reitz⁶ showed that the pH value obtained when a bicyclobutane solution was added to a methanolic solution of $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ depended upon the rate of addition of the hydrocarbon. The results of a similar study with substituted bicyclobutanes are reported in Table II. As the rate of addi-

Table II. Reaction of Bicyclobutanes and $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ in Methanol

Reactants	Products and reaction conditions (%)		
	I ^a	II ^b	III ^c
1	3 (49)	3 (35)	3 (5)
	4 (51)	4 (65)	4 (95)
5	6 (71)	6 (70)	6 (34)
	7 (13)	7 (14)	7 (13)
	8 (16)	8 (16)	8 (53)
	10 (83)	10 (75)	10 (18)
12	11 (17)	11 (25)	11 (72)
	13 (75)	13 (62)	13 (2)
	14 (20)	14 (18)	14 (1)
	15 (0)	15 (0)	15 (0)
	12 (5)	12 (20)	12 (97)

^a Reactions were carried out by dropwise addition (~1 drop every 12 sec) of a solution of bicyclobutane (~0.05 ml) and 2 ml of methanol to a solution of 8 mg of $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ and 3 ml of methanol. Products were analyzed by vpc. ^b Rate of addition of the bicyclobutane solution was decreased to about one drop every minute. ^c Rate of addition was the same as in footnote b with 20 mg of NaHCO_3 present.

tion of the bicyclobutane solution was decreased, larger amounts of diene were formed; the presence of NaHCO_3 also increased the amount of dienes formed.

(6) P. G. Gassman and R. R. Reitz, *J. Amer. Chem. Soc.*, **95**, 3057 (1973).