J. Am. Chem. Soc. **1981**, *103*, 2783-2791

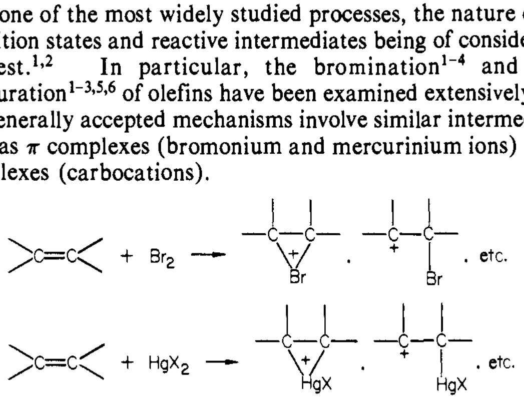
Electrophilic Additions to Olefins. A New Approach to Unifying the Mechanisms of Bromination and Oxymercuration

S. Fukuzumi and J. K. Kochi*

Contribution from the Department of Chemistry, Indiana University, Bloomington, Indiana 47405. *Received August 21, 1980*

Abstract: Bromination and oxymercuration of carbon–carbon double bonds represent classical examples of electrophilic addition, but they nonetheless show quite divergent patterns of reactivities for various olefins. However, the olefin reactivities are identical when the differences between the steric effects in the transition states for bromination and oxymercuration are *explicitly* taken into account. Steric terms are developed for olefin–bromine and olefin–mercury(II) interactions from the information included in the charge-transfer (CT) transition energies for the electron donor–acceptor (EDA) complexes. CT absorption spectra of various olefin–mercury(II) complexes are reported for the first time and are compared to the spectra of analogous EDA complexes with bromine. The striking similarity between the activation processes for bromination and oxymercuration, after inclusion of the steric term, derives from a unified mechanism for electrophilic addition to olefins.

In organic chemistry, the electrophilic addition to olefins has been one of the most widely studied processes, the nature of the transition states and reactive intermediates being of considerable interest.[1,2] In particular, the bromination[1-4] and oxymercuration[1-3,5,6] of olefins have been examined extensively, and the generally accepted mechanisms involve similar intermediates such as π complexes (bromonium and mercurinium ions) and σ complexes (carbocations).



Indeed, stable bromonium[7] and mercurinium ions[8] have been observed in media of low nucleophilicity (and the latter in the gas phase[9]), but their existence under reaction conditions is inferred.

In both electrophilic processes, there have been numerous discussions as to whether the transition states are cyclic (π-like) or open (σ-like), as well as their possible interconversion.[1-6] Despite such similar problems, however, there are significant differences in the reactivities of olefins in bromination compared to mercuration. For example, the rates of bromination generally increase with additional methyl substitution at the double bond,[4] whereas mercuration follows the opposite trend.[6b] Such discrepancies have been discussed in terms of differences in the rate-determining steps—that for mercuration being either the formation of the π or σ complexes[10-12] or the subsequent nucleophilic attack (especially by the solvent[6,13]) and that for bromination being the complex formation.[1-4] Generally, a combination of electronic, steric, and solvent effects have been invoked in order to understand the trends in olefin reactivity, although the enormity of the task has been pointed out by Bach and co-workers.[14] No general mechanistic formulation has been brought forth, and the analysis of the reactive intermediates has not succeeded in explaining the significant differences in olefin reactivity between bromination and mercuration.[11,14]

We wish to approach this problem in an entirely different way which stems from the earlier observation of electron donor–acceptor (EDA) complexes between olefins and bromine by Dubois and co-workers.[15,16]

$$>C=C< + Br_2 \rightleftharpoons [>C=C< Br_2]$$

Except for Olah's proposal[17] that the transition state for olefin bromination in nonpolar solvents is akin to the EDA complex, no attempt has been made to exploit its properties in order to understand this electrophilic addition. Moreover, there are no reports of the related EDA complexes to olefins with mercury(II) derivatives, although there are some studies which seem to imply

---

[1] Freeman, F. *Chem. Rev.* **1975**, *75*, 439

[2] (a) Schmid, G. H.; Garratt, D. G. In "Chemistry of Alkenes"; Zabicky, J., Ed.; Wiley-Interscience: New York, 1977; Vol. 3. (b) de la Mare, P. B. D.; Bolton, R. "Electrophilic Additions to Unsaturated Systems"; Elsevier: New York, 1966. (c) Fahey, R. C. *Top. Spectrochem.* **1968**, *3*, 237. (d) Traylor, T. G. *Acc. Chem. Res.* **1969**, *2*, 152. (e) Bolton, R. *Compr. Chem. Kinet.* **1973**, *9*.

[3] (a) Olah, G. A. "Carbocations and Electrophilic Reactions"; Verlag Chemie-Wiley, New York, 1973. (b) Olah, G. A. *Acc. Chem. Res.* **1971**, *4*, 240. (c) Banthorpe, D. V. *Chem. Rev.* **1970**, *70*, 295. (d) Sergeev, G. B.; Serguchev, Yu. A.; Smirnov, V. V. *Russ. Chem. Rev.* (*Engl. Transl.*) **1973**, *42*, 697.

[4] (a) de la Mare, P. B. D. "Electrophilic Halogenation"; Cambridge Unviersity Press: London, 1976. (b) Bienvenue-Goetz, E.; Dubois, J. E. *Tetrahedron* **1978**, *34*, 2021. (c) Hudson, H. R. *Ann. Rep. Prog. Chem., Sect. B* **1978**, *75*.

[5] (a) Seyferth, D. *J. Organomet. Chem.* **1979**, *183*, 141. (b) Wardell, J. L., in *Organomet. Chem.* **1979**, *7*, 26. Chatt, J. *Chem. Rev.* **1951**, *48*, 7. (d) Matteson, D. S. "Organometallic Reaction Mechanisms of the Nontransition Elements", Academic Press: New York, 1974; pp 202.

[6] (a) Kitching, W. *Organomet. Chem. Rev.* **1968**, *3*, 61. (b) Kitching, W. In "Organometallic Reactions"; Becker, E. I., Tsutsui, M. Eds.; Wiley-Interscience: New York, 1972; p 319.

[7] (a) Bollinger, J. M.; Brinich, J. M.; Olah, G. A. *J. Am. Chem. Soc.* **1970**, *92*, 4025. (b) Olah, G. A.; Schilling, P.; Westerman, P.; Lin, H. C. *Ibid.* **1974**, *96*, 3581. (c) Olah, G. A.; Westerman, P.; Melby, E. G.; Mo, Y. K. *Ibid.* **1974**, *96*, 3565.

[8] (a) Olah, G. A.; Clifford, P. R. *J. Am. Chem. Soc.* **1971**, *93*, 1261, 2320; **1973**, *95*, 6067. (b) Olah, G. A.; Yu, S. H. *J. Org. Chem.* **1975**, *40*, 3638. (c) Hodjat-Kachani, H.; Lattes, A.; Perie, J. J.; Roussel, J. *J. Organomet. Chem.* **1975**, *96*, 175.

[9] (a) Bach, R. D.; Gauglhofer, J.; Kevan, L. *J. Am. Chem. Soc.* **1972**, *94*, 6860. (b) Bach, R. D.; Patane, J.; Kevan, L. *J. Org. Chem.* **1975**, *40*, 257.

[10] (a) Brown, H. C.; Geoghegan, P. J. *J. Org. Chem.* **1972**, *37*, 1937. (b) Bergmann, H. J.; Collin, G.; Just, G.; Muller-Hagen, G.; Pritzkow, W. *J. Prakt. Chem.* **1972**, *314*, 285.

[11] Ambidge, I. C.; Dwight, S. K.; Rynard, C. M.; Tidwell, T. T. *Can. J. Chem.* **1977**, *55*, 3086.

[12] (a) Abley, P.; Byrd, J. E.; Halpern, J. *J. Am. Chem. Soc.* **1973**, *95*, 2591. (b) Shinoda, S.; Isemura, M.; Saito, Y. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 1855. (c) Barrelle, M.; Apparu, M. *Tetrahedron* **1977**, *33*, 1309. (d) Chaudhuri, A. K.; Das, M. N. *Ibid.* **1965**, *21*, 457. (e) Kreshkov, A. P.; Balyatinskaya, L. N.; Chesnokova, M. *Zh. Obshch. Khim.* **1973**, *43*, 166.

[13] (a) Bach, R. D.; Richter, R. F. *Tetrahedron Lett.* **1973**, 4099. (b) Bach, R. D.; Richter, R. F. *J. Org. Chem.* **1973**, *38*, 3422. (c) Cristol, S. J.; Perry, J. S., Jr.; Beckley, R. S. *J. Org. Chem.* **1976**, *41*, 1912.

[14] Bach, R. D.; Weibel, A.; Patane, J.; Kevan, L. *J. Am. Chem. Soc.* **1976**, *98*, 6237.

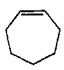
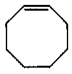
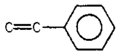
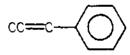
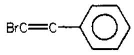
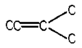
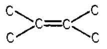
[15] Dubois, J. E.; Garnier, F. *Spectrochim. Acta., Part A* **1967**, *23A*, 2279; *Tetrahedron Lett.* **1965**, 3961; *J. Chim. Phys.* **1966**, *63*, 351.

[16] See also: (a) Buckles, R. E.; Yuk, J. P. *J. Am. Chem. Soc.* **1953**, *75*, 5048. (b) Mayo, F. R.; Katz, J. J. *J. Am. Chem. Soc.* **1947**, *69*, 1339. (c) Lishnevskii, V. A.; Sergeev, G. B. *Kinet. Katal.* **1964**, *5*, 407.

[17] Olah, G. A.; Hockswender, T. R., Jr. *J. Am. Chem. Soc.* **1974**, *96*, 3574.

0002-7863/81/1503-2783$01.25/0

Table I. Charge-Transfer Transition Energies for the EDA Complexes of Olefins with Br_2, $HgCl_2$, and $Hg(OAc)_2$

no.	olefin	I_D,[a] eV	$h\nu_{CT}(Br_2)$, eV		$h\nu_{CT}(HgCl_2)$,[g] eV	$h\nu_{CT}(Hg(OAc)_2)$,[g] eV
			e	f		
1	$C{=}CC_3$	9.52	4.56	4.61	5.27	5.08
2	$C{=}CC_4$	9.48	4.54	4.59	5.25	5.06
3	$C{=}CC_6$	9.43[b]	4.54		5.25	5.04
4		8.95[c]	4.16	4.21	4.96	4.80
5		8.81[c]	4.10		4.92	4.78
6		8.97[c]	4.17		4.94	4.84
7		8.42[d]	3.94			
8			3.76			
9			4.12			
10	t-BuC=C	9.45	4.51		5.25	5.08
11	t-BuC=CC trans	8.91	4.10		4.96	4.84
12		8.68		3.97	4.77	4.68
13		8.27		3.61	4.51	4.52

[a] From ref 20a unless stated otherwise. [b] From ref 20b. [c] From ref 20c. [d] From ref 20d. [e] In Freon-113 (from ref 15). [f] In CCl_4. [g] In CH_2Cl_2.

the presence of such complexes.[18] In this study, we have succeeded in observing the charge-transfer (CT) absorption spectra of the EDA complexes of olefins with various mercury(II) derivatives. By using a common series of olefins, we have carefully examined the kinetics of electrophilic bromination and mercuration under the standard reaction conditions required to carry out the comparative analysis of these electrophilic processes.

Results

I. Formation of Olefin Complexes with Bromine and Mercury(II) Electrophiles. Charge-Transfer Absorption Spectra. A. Olefin Complexes with Bromine. When 1-hexene and molecular bromine are mixed in carbon tetrachloride solutions, a new transient absorption is immediately observed in the UV-visible region of the spectrum. The absorption maximum (λ_{max}) is somewhat obscured by the tail absorptions of the solvent and the reactants. However, by measuring the *difference spectrum* under carefully calibrated conditions (see Experimental Section), a single new absorption band can be educed with a distinct maximum at λ_{max} 273 nm, as shown in Figure 1. The validity of the difference spectra was confirmed by showing that the positions and the shapes of the bands were unaltered with changes in the concentrations of the olefins and of bromine. No additional bands could be discerned in the difference spectrum. The charge-transfer[19] spectral data for the series of olefin complexes with bromine in CCl_4 are listed in Table I, together with those reported in Freon-113 (Cl_2FCCF_2Cl) by Dubois and Garnier.[15]

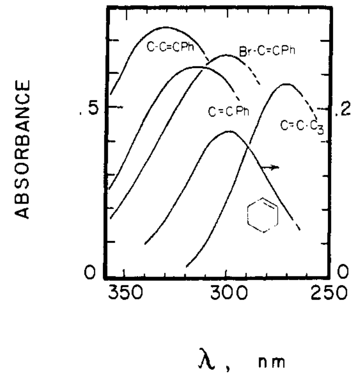


Figure 1. Charge-transfer spectra of olefins with bromine in CCl_4 at 25 °C: [1-pentene] 6.1 × 10^{-2} M, [Br_2] 4.0 × 10^{-2} M; [cyclohexene] 6.6 × 10^{-3} M, [Br_2] 4.0 × 10^{-2} M; [*cis*-β-bromostyrene] 1.5 × 10^{-2} M, [Br_2] 4.0 × 10^{-2} M; [styrene] 5.8 × 10^{-2} M, [Br_2] 8.2 × 10^{-3} M; [β-methylstyrene] 5.1 × 10^{-2} M, [Br_2] 1.3 × 10^{-2} M.

B. Olefin Complexes with Mercury(II) Electrophiles. New transient absorption bands are also observed when the same olefins are treated with mercury(II) compounds such as $HgCl_2$ and $Hg(OAc)_2$ in methylene chloride solution (these mercury(II) derivatives are insoluble in CCl_4). As shown in Figure 2, all are significantly blue shifted relative to those of the corresponding bromine complexes. Thus the overlap of the CT band with the tail absorptions of both $HgCl_2$ and the olefin can be quite severe, and it makes the measurement of the difference spectrum essential for the detection of the olefin–$HgCl_2$ complexes shown in Figure 2a. Similar charge-transfer spectral bands although slightly red shifted are observed with $Hg(OAc)_2$ as shown in Figure 2b,c. Replacement of $HgCl_2$ by $Hg(OAc)_2$ as the electron acceptor makes clearer the presence of a second CT transition, particularly in Figure 2c where the dashed lines represent the Gaussian curves for the two absorption bands of the EDA complex from $Hg(OAc)_2$ and 2,3-dimethyl-2-butene. The relative intensities of these two bands remains invariant with changes in the concentrations of 2,3-dimethyl-2-butene and of $Hg(OAc)_2$. A closer examination of Figure 2b also reveals the presence of a second CT band for the EDA complex of 1-pentene with $Hg(OAc)_2$ as a tail absorption which is absent in the spectrum of the corresponding complex with $HgCl_2$ in Figure 2a. Moreover with electron-rich olefins such as 2,3-dimethyl-2-butene, the red-shift in the EDA complex with

---

(18) (a) Eliezer, I.; Avinur, P., *J. Chem. Soc., Faraday Trans. 2* **1974**, *70*, 1316. (b) Tevault, D.; Nakamoto, K. *Spectrosc. Lett.* **1976**, *9*, 185. (c) Damude, L. C.; Dean, P. A. W. *J. Chem. Soc., Chem. Commun.* **1978**, 1083.

(19) (a) Mulliken, R. S.; Person, W. B. "Molecular Complexes, A Lecture and Reprint Volume"; Wiley-Interscience: New York, 1969. (b) Person, W. B. *J. Am. Chem. Soc.* **1965**, *87*, 167. (c) Mulliken, R. S. *J. Phys. Chem.* **1952**, *56*, 801.

(20) (a) Masclet, P.; Grosjean, D.; Mouvier, G.; Dubois, J. *J. Electron. Spectrosc. Relat. Phenom.* **1973**, *2*, 225. (b) Demeo, D. A.; El-Sayed, M. A. *J. Chem. Phys.* **1970**, *52*, 2622. (c) Remane, H.; Graefe, J.; Herzschuh, R. *Z. Chem.* **1972**, *12*, 194. (d) Rabalais, J. W.; Colton, R. J. *J. Electron Spectrosc. Relat. Phenom.* **1972**, *1*, 83.

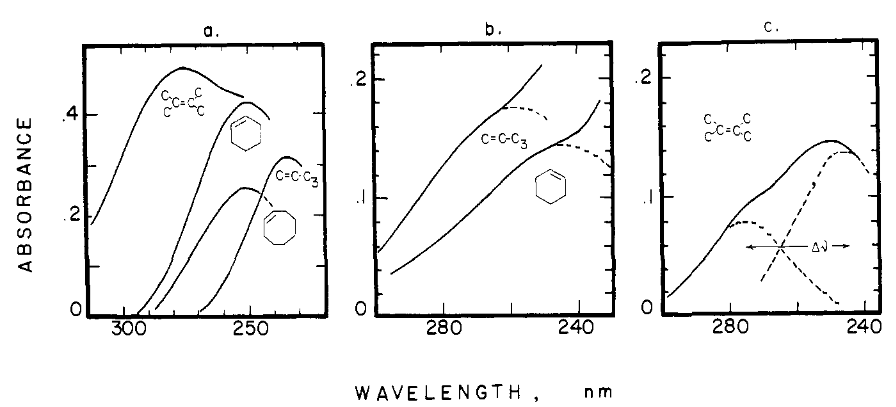


Figure 2. Charge-transfer spectra of olefins with mercury(II) derivatives in CH_2Cl_2 at 25 °C: (a) $HgCl_2$ (5.0×10^{-3} M) with 0.21 M 1-pentene, 5.1×10^{-2} M *cis*-cyclooctene, 0.13 M cyclohexene, and 0.38 M 2,3-dimethyl-2-butene; (b) $Hg(OAc)_2$ (2.0×10^{-3} M) with 6.1×10^{-2} M 1-pentene and 6.5×10^{-2} M cyclohexene; (c) $Hg(OAc)_2$ (2.0×10^{-3} M) and 2,3-dimethyl-2-butene (1.4×10^{-2} M). The dotted curves represent the Gaussian deconvolution.

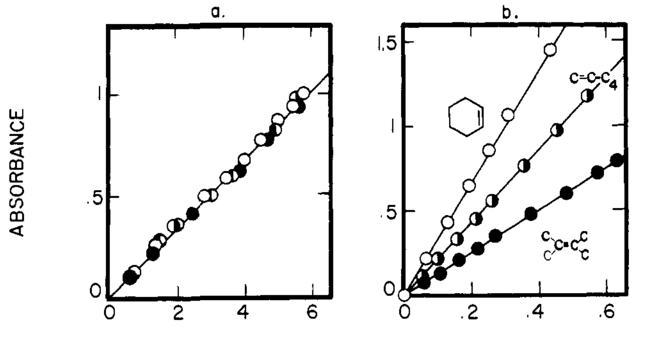


Figure 3. Change in the CT absorbance of (a) the 1-hexene–bromine complex with concentration variations in 1-hexene and Br_2: ○, 2.71×10^{-3} M; ◐, 4.80×10^{-3} M; ●, 1.44×10^{-2} M; ◑, 6.78×10^{-2} M. (b) olefin–$HgCl_2$ complexes with the variation in olefin concentration: ○, cyclohexene measured at 250 nm; ◑, 1-hexene at 236 nm; ●, 2,3-dimethyl-2-butene at 275 nm.

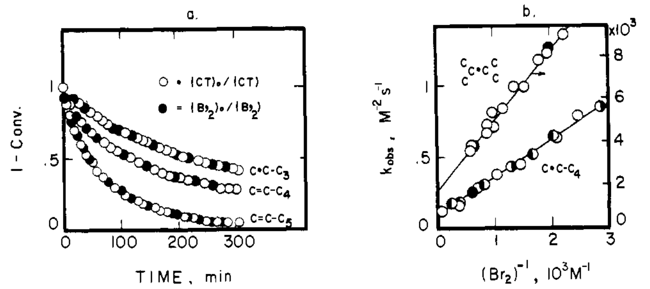


Figure 4. (a) Decay of the CT absorbance (●) and the disappearance of Br_2 (○) during the bromination of olefins in CCl_4 at 25 °C: $[Br_2]_0$ (3.39×10^{-3} M) with 9.08×10^{-2} M 1-pentene, 0.13 M 1-hexene, and 0.104 M 1-octene. (b) Dependence of k_{obsd} on the bromine concentration: (1) 2,3-dimethyl-2-butene under equimolar conditions (○) and the same with 4.9×10^{-3} M isoamyl nitrite as (●); (2) (2) 1-hexene 0.053 M (◐), 0.131 M (○), 0.258 M (◑), 0.131 M (●) with 4.9×10^{-3} M isoamyl nitrite added.

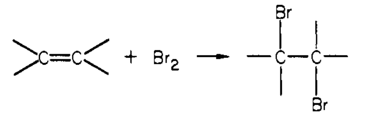
$HgCl_2$ is sufficient to expose the tail of the second CT band as an enhanced absorption below 265 nm (see Figure 2a). A pair of CT bands was also observed for the EDA complexes of other mercury(II) derivatives such as $Hg(CN)_2$, $Hg(O_2CCHMe_2)_2$, $Hg(O_2CCMe_3)_2$, and $Hg(O_2CC_4H_9\text{-}n)_2$ with cyclohexene. (Unfortunately, we were unable to measure the CT spectra of the olefin complexes with $Hg(O_2CCF_3)_2$, owing to the fast rates of adduct formation.[21]) The appearance of two CT bands is a general phenomenon for the EDA complexes of mercury(II), arising from the splitting of the lowest unoccupied orbital in the mercury(II) acceptor as a result of the bending of X–Hg–X in the EDA complex.[22]

C. Formation Constants of Olefin Complexes with Bromine and Mercury(II) Derivatives. The composition of the EDA complexes was established by showing that the absorbance of the CT band increases linearly with the olefin and the bromine concentrations, as illustrated in Figure 3a for 1-hexene. The similar behavior observed with 1-octene, styrene, β-methylstyrene, and *cis*-β-bromostyrene confirms the 1:1 stoichiometry, i.e.

$$>C{=}C< + Br_2 \overset{K_{DA}}{\rightleftharpoons} [>C{=}C< Br_2] \qquad (1)$$

The linearity of the plot in Figure 3a, extending to rather high concentrations of olefin and bromine, indicates that K_{DA} is small (<0.1 M^{-1}),[23] as expected for an EDA complex of bπ–aσ type in accord with Mulliken's classification.[19] The EDA complexes of olefins with the mercury(II) derivatives are also weak, judging from the absence of any significant curvature in Figure 3b, up to 0.5 M olefin concentration.

II. Kinetics of Electrophilic Addition to Olefins. A. Bromination of Olefins. The decay of the transient CT band of the bromine–olefin complexes coincides with bromination according to eq 2.[4] The rates of electrophilic addition were measured in CCl_4



$$>C{=}C< + Br_2 \longrightarrow -\overset{Br}{\underset{|}{\overset{|}{C}}}-\underset{Br}{\overset{|}{\underset{|}{C}}}- \qquad (2)$$

solution by following both the disappearance of the bromine absorption at λ_{max} 415 nm (ε 205.9 M^{-1} cm^{-1}) as well as the decay of the CT absorbance described in the previous section. The diminution of the two different absorption bands occurs in exactly the same manner over the entire course of reaction in the presence of a large excess of olefins, as illustrated in Figure 4a for 1-pentene, 1-hexene, and 1-octene.

The kinetics of olefin bromination in carbon tetrachloride solutions have been variously reported as either second order or third order.[24] Since the kinetics have important bearing on any mechanistic treatment, we have reexamined the bromination of olefins in considerable detail, and the extensive kinetic data are collected in the supplementary materials at different concentrations for various olefins and bromine. The kinetics for olefin bromi-

---

[21] (a) Brown, H. C.; Rei, M.-H.; Liu, K.-T. *J. Am. Chem. Soc.* **1970**, *92*, 1760. (b) Brown, H. C.; Rei, M.-H. *J. Chem. Soc. D* **1969**, 1296.

[22] Fukuzumi, S.; Kochi, J. K. *J. Phys. Chem.* **1981**, *85*, 648.

[23] (a) Benesi, H. A.; Hildebrand, J. H. *J. Am. Chem. Soc.* **1949**, *71*, 2703. (b) Person, W. B. *Ibid.* **1965**, *87*, 167.

[24] (a) Second order: Hanna, J. G.; Siggia, S. *Anal. Chem.* **1965**, *37*, 690. Dubois, J. E.; Garnier, F. *Chem. Commun.* **1968**, 241. (b) Third order: Buckles, R. E.; Miller, J. L.; Thurmaier, J. *J. Org. Chem.* **1967**, *32*, 888. Gebelein, C. G.; Frederick, G. D. *Ibid.* **1972**, *37*, 2211. Sergeev, G. B.; Smirnov, V. V.; Bakarinova, G. A., Vetrova, M. A. *Dokl. Akad. Nauk SSSR* **1972**, *203*, 394. Shilov, E. A.; Sergeev, G. B.; Serguchev, Yu. A.; Smirnov, V. V. *Ukr. Khim. Zhur.* (*Ukr. Ed.*) **1972**, *38*, 1156.

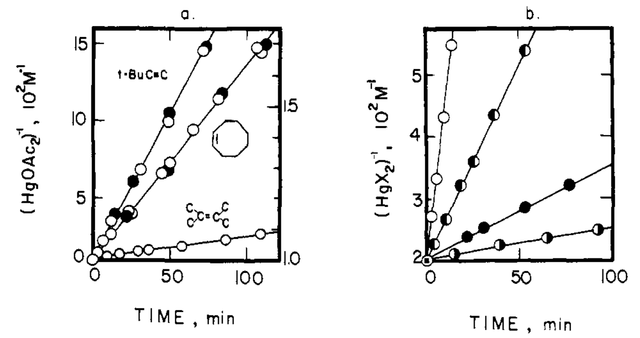


Figure 5. Second-order kinetics for the methyoxymercuration of olefins in methanol at 25 °C: (a) $Hg(OAc)_2$ determined by iodide quench (○) and spectroscopically (●) for 3,3-dimethyl-1-butene, *cis*-cyclooctene, and 2,3-dimethyl-2-butene; (b) *cis*-cyclooctene and (○) $Hg(O_2CCHF_2)_2$, (◐) $Hg(O_2CCHCl_2)_2$, (◑) $Hg(O_2C\text{-}n\text{-}Bu)_2$, (●) $Hg(O_2CCHCl_2)_2$ and 4,4-dimethyl-2-pentene.

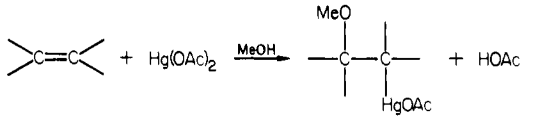
nation in CCl_4 can be expressed as a two-term rate expression[25] (eq 3). The second-order rate constants obtained in this manner

$$-d[Br_2]/dt = k[Br_2][>C{=}C<] + k_3[Br_2]^2[>C{=}C<] \qquad (3)$$

are included in Table II for various olefins, together with those obtained in methanol earlier by Dubois and co-workers[26] for comparison. The values of k in CCl_4 are between 10^6 and 10^7 times smaller than the rate constants in MeOH. Nonetheless, the relative reactivities of various olefins in these solvents are roughly parallel, albeit somewhat attenuated in MeOH (e.g., the ratio of rate constants for 2,3-dimethyl-2-butene and 1-pentene is 1.4×10^4 in MeOH and 7.9×10^4 in CCl_4).[26f] The third-order rate constants k_3 for olefin bromination will be presented later.

At this juncture, it is important to point out the caveat that the bromination of olefins can also proceed via a competing radical-chain processes,[27] and extreme care must be exercised to avoid this complication, especially when it is adventitiously promoted by light. In order to establish that the measured rate of bromination did not include a contribution from a radical chain component, it was shown that the presence of isoamyl nitrite did not retard the rate. The efficacy of this inhibitor was established separately (see Experimental Section), since bromine itself is known to be an excellent chain-transfer agent, i.e., radical trap.[28]

B. Oxymercuration of Olefins. The electrophilic oxymercuration of olefins consists of the mixed addition of the mercuric salt and a protic solvent such as methanol to the olefin according to eq 4.[5] The rate of methoxymercuration of various



$$>C{=}C< + Hg(OAc)_2 \xrightarrow{MeOH} -\overset{MeO}{\overset{|}{C}}-\underset{HgOAc}{\underset{|}{C}}- + HOAc \qquad (4)$$

olefins shown in Figure 5a was followed in methanol by monitoring the disappearance of $Hg(OAc)_2$ both spectrophotometrically[11] and by quenching with iodide,[29] as described in detail in the Experimental Section. The kinetics of methoxymercuration, are expressed by the second-order rate expression in eq 5. The second-order rate constants k obtained by the two independent procedures are shown to be in excellent agreement in Figure 5a, and they are also listed in Table II.

$$-d[Hg(OAc)_2]/dt = k[>C{=}C<][Hg(OAc)_2] \qquad (5)$$

Table II. Second-Order Rate Constants for the Bromination and the Mercuration of Olefins[a]

olefin no.	bromination log k (CCl_4)	bromination log k (MeOH)[b]	mercuration log k (MeOH)
1	−4.38	2.65	1.26
2	−3.59	2.67	1.34
3	−3.21		1.30
4	−1.96	4.05	0.26
5	−0.72	5.00	0.11
6	−0.70	2.82	−2.28
7	−3.49	3.18	0.43
8	−3.66	2.90	−2.04
9	−6.60		−4.28
10	−4.77	1.98	−0.80
11	−1.25	3.04	−3.00[d]
12	−0.62	6.11[c]	0.83
13	0.52	6.80	−1.96

[a] At 25 °C. [b] Taken from ref 26 log k given in $M^{-1}\ s^{-1}$. [c] Taken from ref 4b. [d] Cis and trans mixture.

Table III. Reactivity of Various Mercury(II) Derivatives in the Oxymercuration of *cis*-Cyclooctene and *trans*-4,4-Dimethyl-2-Pentene[a]

Hg(II) deriv	E_A,[b] eV	second-order rate constant, $M^{-1}\ s^{-1}$ cyclooctene	second-order rate constant, $M^{-1}\ s^{-1}$ *t*-BuC=CC
$HgCl_2$	0.71	*c*	*c*
$Hg(O_2CMe)_2$	0.71	5.2×10^{-3}	3.8×10^{-3}
$Hg(O_2CCHMe_2)_2$	0.74	4.4×10^{-3}	3.6×10^{-3}
$Hg(O_2CCMe_3)_2$	0.74	2.2×10^{-3}	2.6×10^{-3}
$Hg(O_2C\text{-}n\text{-}Bu)_2$	0.75	2.8×10^{-3}	1.3×10^{-3}
$Hg(O_2CCH_2Cl)_2$	0.78	5.3×10^{-2}	1.1×10^{-2}
$Hg(O_2CCHCl_2)_2$	0.75	3.8×10^{-2}	8.3×10^{-3}
$Hg(O_2CCHF_2)_2$	0.84	0.21	9.5×10^{-2}
$Hg(O_2CCF_3)_2$	1.00	0.96	0.23
Br_2	1.48	6.6×10^2	1.1×10^3

[a] In MeOH at 25 °C. [b] Electron affinity, see Experimental Section. [c] Too slow to determine accurately.

Since the rate of methoxymercuration is highly dependent on the ligands, the reactivities of various mercury(II) electrophiles were examined in methanol with a common olefin. Second-order kinetics (as in eq 5) were established for the addition of each of these mercury(II) derivatives to cyclooctene and 4,4-dimethyl-2-pentene, as illustrated in Figure 5b. (The rates of methoxymercuration of olefins with $HgCl_2$ and $HgBr_2$ were too slow to measure reliably.) The second-order rate constants are listed in Table III, together with the electron affinities of various mercury(II) derivatives. The rates of mercuration in nonpolar solvents such as methylene chloride are too slow to measure reliably, even with the relatively reactive olefins such as 1-hexene and 1-octene. The strong solvent dependence of mercuration is thus akin to that described for bromination in Table II. A third-order component was not observed in the kinetics of oxymercuration under these conditions.

Discussion

The availability of kinetic data for the bromination and oxymercuration of a common series of olefins under the same reaction conditions allows a direct comparison of these electrophilic ad-

---

[25] (a) In a solvent of intermediate polarity such as acetic acid, the combination of second- and third-order kinetics in eq 3 has been well established: Yates, K.; McDonald, R. S.; Shapiro, S. A. *J. Org. Chem.* **1973**, *38*, 2460. Schmid, G. H.; Modro, A.; Yates, K. *Ibid.* **1980**, *45*, 665. (b) In eq 3, the second-order rate constant k is given as the slope and the third-order rate constant k_3 as the intercept in Figure 4b where $k_{obsd} = (k/[Br_2]) + k_3$.

[26] (a) Dubois, J. E.; Mouvier, G. *Tetrahedron Lett.* **1963**, 1325. (b) Dubois, J. E.; Alcais, P.; Barbier, G. *J. Electroanal. Chem.* **1964**, *8*, 359. (c) Ruasse, M. F.; Dubois, J. E.; Argile, A. *J. Org. Chem.* **1979**, *44*, 1173. (d) Dubois, J. E.; Bienvenue-Goetz, E. *Bull. Soc. Chim. Fr.* **1968**, *2089*. (e) Dubois, J. E.; Huynh, X. Q. *Tetrahedron Lett.* **1971**, 3369. (f) Note that the reactivity patterns determined directly in CCl_4 from the rate constants in Table II differ from those evaluated by the competition method in Freon 113.[17]

[27] (a) Poutsma, M. L. *J. Am. Chem. Soc.* **1963**, *85*, 3511; **1965**, *87*, 2161, 2172. (b) Imoto, M.; Sato, T.; Takemoto, K. *Makromol. Chem.* **1966**, *95*, 117; **1967**, *104*, 297. (c) Miller, W. T., Jr.; Koch, S. D., Jr.; McLafferty, F. W. *J. Am. Chem. Soc.* **1956**, *78*, 4492. (d) Shellhamer, D. F.; Heasley, V. L.; Foster, J. E.; Luttrull, J. K.; Heasley, G. E. *J. Org. Chem.* **1977**, *42*, 2141. (e) Shellhamer, D. F.; Oakes, M. L. *Ibid.* **1978**, *43*, 1316.

[28] Chambers, R. L.; Jensen, F. R. In "Aspects of Mechanism and Organometallic Chemistry"; Brewster, J., Ed.; Plenum Press: New York, 1978.

[29] Abraham, M. H.; Johnston, G. F.; Spalding, T. R. *J. Inorg. Nucl. Chem.* **1968**, *30*, 2167.

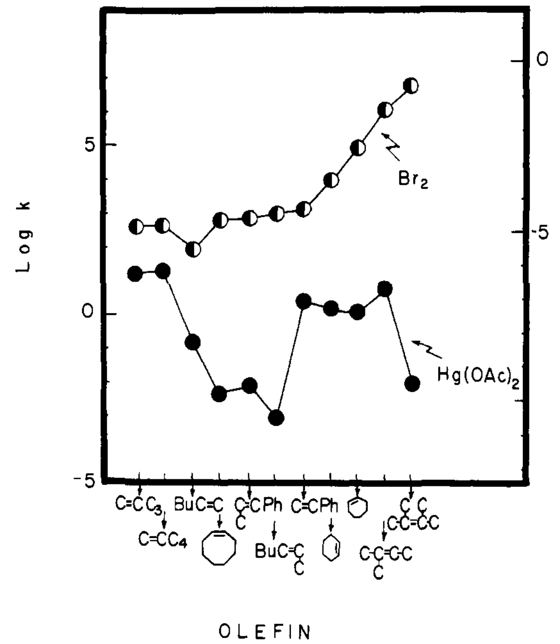


Figure 6. Comparison of the reactivities of various olefins in oxymercuration with use of $Hg(OAc)_2$ and (●) with electrophilic bromination (◐) in methanol.

ditions to be made. Thus the second-order rate constants (log *k*) for the bromination of the structurally diverse olefins are compared in Figure 6 to the rate constants for methoxymercuration in methanol, as listed in Table II. Clearly, the reactivity patterns of the olefins are quite different for these processes—*the two generally following opposite trends*. The relative rates of bromination increase with the donor property of the olefin as measured by its ionization potential. On the other hand, the relative rates of oxymercuration show little correlation with bromination, let alone the ionization potentials of the olefins—the most electron-rich, 2,3-dimethyl-2-butene, actually reacting substantially slower than the reference 1-pentene.

Let us now focus on the reactivity patterns arising from structural variations of the electrophiles, including bromine and the various mercury(II) derivatives, by relating the rates of addition to the acceptor abilities of the electrophile. Thus the second-order rate constants for electrophilic addition to *t*-$BuCH{=}CHCH_3$ listed in Table III is plotted in Figure 7 which an acceptor property of the electrophile such as its electron affinity.[30] The linear correlation in Figure 7, which includes bromine together with all the mercury(II) derivatives, suggests that a strong similarity exists between the transition states for mercuration and the transition state for bromination. A similar linear correlation also occurs with the same slope in the bromination and oxymercurations of *cis*-cyclooctene.

I. The Mechanistic Problem. The kinetic results presented in this study can be summarized by raising the question: "Why do bromination and oxymercuration correlate with the acceptor ability of the electrophile (Figure 7) but show divergent trends with the donor ability of the olefin (Figure 6)?" It may be tempting to simply brush such a question aside since it is obvious that bromine and mercury(II) derivatives are so structurally diverse as to resist any correlation of their behavior. However, we recognize that steric effects which are known to play an important role in bromination[31] certainly cannot be expected to be the same for oxymercuration. Indeed the diverse patterns of reactivity for bromination and oxymercuration, similar to those presented in Figure 6, have been noted and qualitatively attributed to the dominance of steric effects in oxymercuration,[11] since it actually leads to a decreasing reactivity with increasing donor properties of the olefin.

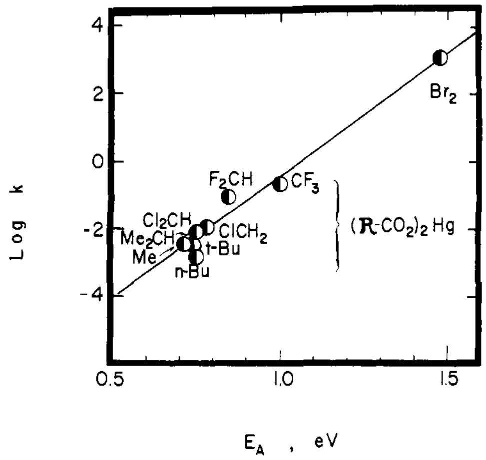
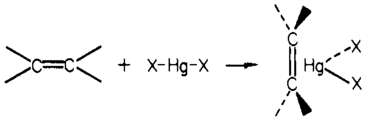


Figure 7. Reactivities of bromine and various mercury(II) derivatives with 4,4-dimethyl-2-pentene as a function of the electron affinity of the electrophile.

Previous treatments of steric effects have relied on the use of the additivity of empirical parameters such as the Taft E_s constants.[32] It should be realized, however, that these treatments only take into account the variations in the olefin donor and do not explicitly include effects arising from the bromine or mercury(II) electrophile. In order to include steric effects in the olefin as well as the electrophile simultaneously, we deemed it necessary to obtain information specifically relating to the *mutual* interaction between these moieties—such as those derived from complex formation. Thus the observation of transient EDA complexes of olefins with both bromine and mercury(II) derivatives, as reported in this study, provides us with a unique opportunity to compare these properties and relate them to the transition states for electrophilic addition. In order to do so, we first describe how steric effects arising from olefin-electrophile interactions can be quantitatively extracted from the informaton provided by the EDA complexes.

II. Quantitative Evaluation of Steric Effects from EDA Complexes. Steric effects in EDA complexes are manifested in the main separation r_{DA}, which is the parameter reflecting the close appproach of the electrophile to the olefin. Indeed the bending of the linear X–Hg–X in the formation of the olefin complex, i.e.



(6)

as shown by the multiple absorptions in Figure 2, attests to the intimate inner-sphere character of these EDA complexes.[22] The relative steric effects in these complexes can be evaluated from the positions of the CT absorption bands ($h\nu_{CT}$), the ionization potential (I_D) of the olefin and the electron affinity (E_A) of the electrophile.[33] For a given electrophile interacting with a series of olefins, the relative steric effect is given by[34]

$$\Delta E = -\Delta I_D + \Delta h\nu_{CT} \tag{7}$$

where ΔI_D is the difference in the ionization potential between a given olefin and a reference olefin and $\Delta h\nu_{CT}$ is the difference in their CT energies listed in Table I. For the reference olefin, the least hindered compound in this study is arbitrarily chosen as 1-pentene.

Since we are particularly concerned with the changes in reactivity with structural differences, the steric term ΔE in eq 7 is

---

(30) For the evaluation of electron affinities, see the Experimental Section.

(31) Grosjean, D.; Mouvier, G.; Dubois, J. E. *J. Org. Chem.* **1976**, *41*, 3872.

(32) (a) Shorter, J. *Adv. Linear Free Energy Relat.* **1972**, Chapter 2. (b) Exner, O. in *Correl. Anal. Chem.: Recent Adv.* **1978**, Chapter 10. (c) These treatments of the additivity of steric effects differ from that evaluated by $\mathcal{E}$ in that the latter no doubt includes cross terms from the olefin and electrophile parameters.

(33) Fukuzumi, S.; Kochi, J. K. *J. Phys. Chem.* **1980**, *84*, 608.

(34) To avoid disruption of the continuity, the origin of eq 7 is presented at the end of the paper. See also ref 33.

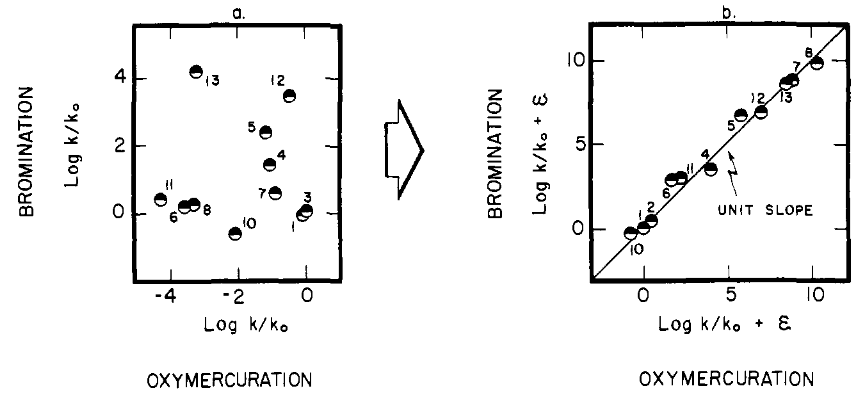


Figure 8. Direct comparison of the relative reactivity of olefins in mercuration and bromination: (a) before and (b) after inclusion in the steric effects. The line is arbitrarily drawn with a slope of unity to emphasize the fit to eq 8. The solvent is methanol.

Table IV. Steric Terms ℰ for Various Olefins with Br_2, $Hg(OAc)_2$, and $HgCl_2$[a]

olefin no.	$\mathcal{E}_{Br_2}$	$\mathcal{E}_{Hg(OAc)_2}$	$\mathcal{E}_{HgCl_2}$	$-\Sigma E_s$[b]
1	0	0	0	−3.36 (0)
2	0.4	0.4	0.4	−3.33 (0.03)
3	1.2	0.9	1.2	−3.32 (0.04)
4	3.0	5.1	4.5	
5	4.3	7.0	6.2	
6	2.8	5.3	3.8	
7	8.2	9.7[c]	7.8[d]	
8	9.5	13.7[c]	9.5[c]	
10	0.4	1.3	0.9	−2.18 (1.18)
11	2.6	6.4	5.2	−0.94 (2.42)
12	3.4	7.5	5.8	−1.24 (2.12)
13	4.3	11.7	8.3	0 (3.36)

[a] $\mathcal{E} = \Delta E/2.3RT$ (unitless), ΔE obtained from eq 7 and the data in Table I. [b] Summation of Taft steric constants (ref 32) with signs reverse. The values in parentheses are relative to 1-pentene for comparison with ℰ. [c] The values of $h\nu_{CT}$ are extrapolated from the relationship between I_D and $h\nu_{CT}$ observed with other olefins.

converted from an energy term to a scale common with the rate constant ln k, viz., $\mathcal{E} = \Delta E/2.3RT$, which is tabulated in Table IV for bromine and various mercury(II) electrophiles. Several features in Table IV are noteworthy. Most importantly, there is no simple relationship between ℰ for bromine and ℰ for mercury(II) complexes. Thus the steric term cannot be uniformly derived by a direct additivity of steric parameters such as the summation of Taft constants $\sum E_s$ presented in the last column of Table IV. There is however a general trend for ℰ in mercury(II) complexes to be significantly larger than ℰ in bromine complexes, particularly for the most sterically hindered olefins such as trimethyl- and tetramethylethylene.

III. Quantitative Comparison of Electrophilic Bromination and Oxymercuration of Olefins—A Unified View. The relative reactivity of various olefins in electrophilic bromination is given by $\log (k/k_0)_{Br_2}$ where k_0 refers to the reference 1-pentene, and it is compared directly with the relative reactivity in oxymercuration $\log (k/k_0)_{HgX_2}$ in Figure 8a. The random, "buckshot" appearance of the plot encourages no correlation between these two electrophilic processes. However, if the steric term evaluated independently as ℰ in Table IV is simply included in with the relative reactivity, the remarkable transformation of the data is shown in Figure 8b. The linear correlation in Figure 8b is expressed by eq 8. In other words, *when the steric terms for the olefin–bromine*

$$\log (k/k_0)_{Br_2} + \mathcal{E}_{Br_2} = \log (k/k_0)_{HgX_2} + \mathcal{E}_{HgX_2} \qquad (8)$$

and olefin-mercury(II) interactions are included, the relative reactivities of various olefins to electrophilic bromination and mercuration are identical. We interpret such an unprecedented relationship to signify that related transition states are actually involved in these apparently dissimilar process (vide infra). As a corollary to this conclusion, the relative reactivities in bromination and oxymercuration are expected to be the same in the absence of steric differences among olefins. Indeed this prediction is borne out with a series of para-substituted styrenes that show quite similar reactivity trends in bromination and oxymercuration.[35]

The success of this interrelationship depends on our ability to evaluate the steric term arising from the mutual interaction of the olefin with the electrophile, be it bromine or a mercury(II) derivative. This treatment differs significantly from earlier attempts to correlate the reactivity of olefins in electrophilic additions. Although it is generally recognized that steric effects can be distinguished from polar effects in linear free-energy relationships, the approach has been largely empirical.[32] Indeed, the rate constants for bromination have been extensively analyzed in terms of Taft polar (σ^*) and steric (E_s) parameters, the relative contributions of each depending on the substitution and the topological pattern about the double bond.[31] However, in order to carry out a similar Hammett–Taft type of analysis for oxymercuration, Pritzkow and co-workers[36] were forced to exploy four parameters to develop a reliable correlation. On the other hand, the direct relationship between electrophilic bromination and mercuration in Figure 8b evolves naturally from the experimental data by a purely operational approach with use of steric effects as evaluated by eq 7. (For the interested reader, the reason why the charge-transfer formulation in eq 7 can be used, is presented separately at the end of this paper.)

Summary and Conclusions

The reactivities of various olefins in electrophilic bromination, as measured by the second-order rate constants for addition, show no relationship to oxymercuration in the same solvent. Although there is a general trend for olefins to react with bromine according to their donor ability, no such relationship holds for oxymercuration, in which the electron-rich 2,3-dimethyl-2-butene is actually less reactive than 1-pentene. The difference is traced to intermolecular steric effects which are significantly larger in the transition state for mercuration compared to that of bromination.

Steric effects in electrophilic additions to olefins are evaluated directly from the properties of the electron donor–acceptor (EDA) complexes of olefins with bromine and with various mercury(II) derivatives. The mutual interaction of olefins with these electrophiles leads to steric effects which parallel those present in the transition states for electrophilic addition. The evaluation of steric effects in this manner differs in a significant manner from the earlier treatments which depend heavily on the additivity of em-

---

(35) The Hammett ρ value for the rates of mercuration of para-substituted styrenes has recently been reported to be −3.2 (Lewis, A.; Azoro, J. *Tetrahedron Lett.* **1979**, 3627). This value compares with the corresponding ρ value of −4.2 for the rates of bromination of a similar series of para-substituted styrenes (Rolston, J. H.; Yates, K. *J. Am. Chem. Soc.* **1969**, *91*, 1483). See also: Dubois, J. E.; Schwartz, A. *Tetrahedron Lett.* **1964**, 2167.

(36) Bergmann, H. J.; Collin, G.; Just, G.; Muller-Hagen, G.; Pritzkow, W. *J. Prakt. Chem.* **1972**, *314*, 285.

pirical parameters. Furthermore the phenomenological treatment of steric effects by the use of charge-transfer transition energies can encompass a wide range of intermolecular interactions which cannot be approximated by a linear free-energy treatment of substituent constants[32] since it explicitly includes the electrophile as well as the olefin. The steric effect can be evaluated for many olefins, being limited only by the observation of the charge-transfer band. Although we have restricted ourselves to a common solvent in this study, the charge-transfer formulation also allows solvent effects to be included.[37] Most importantly, the operational utility of exploiting the properties of EDA complexes to obtain quantitative measures of steric effects in transition states will provide a direct and general method for interrelating various other electrophilic additions to olefins in a unified manner.

Experimental Section

Materials. All olefins used in this study are commercially available and were distilled from sodium prior to use. Bromine (reagent grade, Fisher Scientific Corp.) was refluxed with solid KBr and distilled from P_2O_5. Fresh standard solutions of bromine were prepared by vacuum transfer into a dry, glass-stoppered bottle in which carbon tetrachloride was introduced in the dark under argon. The concentrations of the standard solutions of bromine were frequently checked spectroscopically, and the purification procedure was repeated whenever the concentrations were varied. The mercury derivatives used in this study [$HgCl_2$, $Hg(O_2CMe)_2$, $Hg(O_2CCHMe_2)_2$, $Hg(O_2CCMe_3)_2$, $Hg(O_2C\text{-}n\text{-}Bu)_2$, $Hg(O_2CCH_2Cl)_2$, $Hg(O_2CCHCl_2)_2$, $Hg(O_2CCHF_2)_2$, and $Hg(O_2CCF_3)_2$] were described previously.[38] Fresh aliquots of the mercury(II) solutions were made up for each spectral measurement to avoid complications from possible solvolyses. The solvents, methanol, methylene chloride, and carbon tetrachloride, were obtained commercially and purified according to standard methods.[39]

Spectral Measurements of the CT Absortion Bands. (a) Bromine has an absorption at λ_{max} 415 nm with ϵ_{max} 205.9 M^{-1} cm^{-1} in carbon tetrachloride[24b] but does not have significant absorbance in the region between 270 and 330 nm. When a known amount of olefin (10^{-2} - 10^{-1} M) was added to the bromine solution (10^{-3} - 10^{-2} M), a new transient absorption appeared in the region between 270 and 330 nm. The stability and the position of the new absorption depended on the olefin. For terminal olefins such as 1-pentene, 1-hexene, and 1-octene, the CT absorbances were sufficiently persistent to allow slow spectral scans. However, the absorption maxima were somewhat obscured by the absorptions due to the solvent (carbon tetrachloride) and bromine. Therefore, the validity of the absorption maxima was confirmed by measuring the difference spectra under calibrated conditions with use of a Cary 14 spectrophotometer with the compartment thermostated at 25 °C.[33] In a typical procedure, the spectrum of the bromine solution was first measured against a reference consisting of the same solvent by using a matched pair of 10-mm quartz cuvettes. Next, the spectrum of the solution of the olefin and bromine was measured against the reference containing the olefin at the same concentration. The first spectrum was subtracted from the second to afford the spectrum of the CT absorption for the EDA complex of the olefin with bromine.

All transfers were effected with glass pipets to prevent contamination from trace metal impurities and were carried out in the dark to avoid photochemical reactions. It was also confirmed that the monitoring light from the spectrometer did not affect the measurements of the CT absorbance. The stability of the absorbance in the presence of the monitoring light was the same as that obtained in its absence, as periodically checked by shuttering the light of the spectrophotometer. For more reactive olefins such as cyclohexene, cycloheptene, and *cis*-cyclooctene, the absorption spectra decreased measurably within a few minutes, which necessitated the rapid measurement of the spectrum. However, the absorption maxima could be determined accurately by choosing lower bromine concentrations (10^{-3} M) in which the absorbance was more persistent.

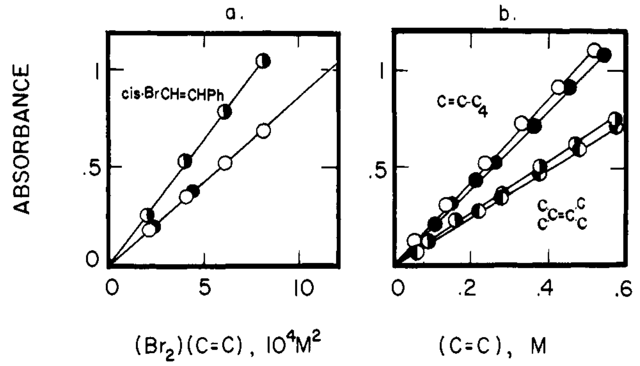


Figure 9. Temperature dependence of the CT absorbance: (a) Br_2 complex with *cis*-β-bromostyrene $[Br_2]_0$ 4.0×10^{-2} M at 25 °C (○) and (◑) 8.2×10^{-3} M at 25 °C; (b) $HgCl_2$ complex with 1-hexene (240 nm) at 8 (○) and at 25 °C (●), with 2,3-dimethyl-2-butene (275 nm) (◑) at 8 and 25 °C and $[HgCl_2]_0$ 5.0×10^{-3} M (◐) in CH_2Cl_2.

(b) Mercury Derivatives have absorptions in the UV region with high extinction coefficients, typically, λ_{max} 206 nm, ϵ_{max} 4000 in methanol.[22] The tail of the absorption is significant above 240 nm in the concentration range of the mercury derivatives studied (2.0×10^{-2} M). The olefin compounds also have tail absorptions in the region of interest. Therefore, in order to bring forth the CT spectra, it was essential to measure the difference spectra as described above. The maximum concentrations of the olefin and mercury derivatives were limited to below that which would cause the slit width of the spectrometer to open to its maximum (3.0 mm). In most cases, the use of (2–5) $\times 10^{-3}$ M of the mercury derivative and 10^{-2} M of olefin in methylene chloride afforded the optimum conditions to observe clear absorption maxima of the EDA complexes. In each case, the absorption maximum was determined under the conditions in which λ_{max} remained constant with changes in the concentration of the olefin. The observed λ_{max} varied with the concentration of olefin at higher concentrations ($>10^{-1}$ M) as a result of the rapid change of the slit width. For the EDA complexes of olefins and $HgCl_2$ in methylene chloride, the CT absorbance was stable, and no change of the spectra was observed during repeated slow scans. For the other mercury(II) complexes with olefins (e.g., $Hg(OAc)_2$ in methylene chloride) the absorption at the lower wavelengths ($\sim$240 nm) increased gradually with time, owing to the formation of the products with much higher extinction coefficients, and it necessitated the expeditious measurement of the spectrum.

Formation Constants of the EDA Complexes. In most cases, the evaluations of the formation constants for the EDA complexes of olefins with bromine and mercury derivatives based on Benesi–Hildebrand plot[23] were not successful because of the small formation constants. For the EDA complexes of cyclohexene and $HgCl_2$ in methanol, the curvature in the plot between the CT absorbance and the concentrations of the olefin allowed us to estimate the formation constant as 0.8 ± 0.1 M^{-1} at 25 °C. The use of three different wavelengths (250, 260, and 265 nm) and different concentrations of $HgCl_2$ (2.0×10^{-2} and 5.0×10^{-3} M) for the Benesi–Hildebrand plots gave the same value within the experimental error mentioned above. The formation constants for the other olefin complexes are 0.4 ± 0.1 (cycloheptene) and 0.4 ± 0.1 (*cis*-cyclooctene).

The weakness of these EDA complexes was further confirmed by the temperature dependence of the CT absorbance. For the $HgCl_2$ complexes with 1-hexene and 2,3-dimethyl-2-butene in methylene chloride, their CT absorbances increased slightly with a decrease of the temperature from 25 to 8 °C as illustrated in Figure 9. The heats of formation of the $HgCl_2$ complexes with 1-hexene and 2,3-dimethyl-2-butene were estimated to be 0.8 and 0.6 kcal mol^{-1}, respectively, assuming that the extinction coefficients are temperature independent.

Kinetic Measurements. (a) The rate of bromination of olefins in carbon tetrachloride was followed by the disapppearance of the bromine absorbance (λ_{max} 415 nm, ϵ_{max} 205.9 M^{-1} cm^{-1}), as well as the decay of the CT absorbance. A stock solution of bromine in CCl_4 was freshly prepared from purified bromine under argon, and the kinetic study was carried out in a Schlenk tube equipped with a small side arm fused to a square quartz cuvette. It was placed in the thermostated compartment (at 25 °C) of a Cary 14 spectrophotometer. A 3.0-mL aliquot of a stock bromine solution was introduced with a glass pipet, and an appropriate amount of a olefin (1–100 μL) was transferred to the side arm under argon. The two solutions were mixed by shaking the Schlenk cell vigorously for a few seconds and the spectrum recorded immediately. For the less reactive olefins such as the terminal olefins, the reactions were

---

[37] (a) The direct comparison in Figure 8 is carried out in a common solvent (methanol) to minimize solvent effects. The insolubility of $HgCl_2$ precluded a similar comparison of oxymercuration with bromination in the less polar CCl_4. The importance of solvation should be noted in values of *k*(bromination) which are at least 10^6 times faster in methanol than those in CCl_4, as shown in Table II. (b) In order to treat solvent effects quantitatively, it is essential to have a knowledge of the solvation energy of the olefin cation radical (studies in progress), as shown previously in the related electrophilic cleavage of alkylmetals. The solvent effects have been analyzed quantitatively as a result of the independent determination of the solvation energy of the alkylmetal cation radical: Fukuzumi, S.; Kochi, J. K. *J. Phys. Chem.* **1980**, *84*, 2246, 2254. Reference 38.

[38] Fukuzumi, S.; Kochi, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 7290.

[39] Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. "Purification of Laboratory Chemicals"; Pergamon Press: Elmsford, NY, 1966.

carried out with a large excess of olefins, which allowed the disappearance of the CT absorbance as well as the bromine absorbance to be monitored simultaneously. For the more reactive olefins such as cycloolefins and 2,3-dimethyl-2-butene, the reactions were carried out with use of equimolar amount of Br_2 and olefins, and only the bromine absorbance was monitored. It was confirmed that there was no interference from species such as Br_3^- ($\epsilon_{Br_3^-}$ 777 at 390 nm)[40] since the change of the ratio of the absorbance change during the reaction relative to the initial value, i.e. $(A - A_\infty)/A_0$, was independent of the wavelength used to monitor the reaction. It was also shown that the observed rate was unaffected by the monitoring light by periodically shuttering the spectrophotometer.

(b) Oxymercuraton of olefins by mercury(II) derivatives was carried out in 10-mm quartz curvettes placed in the thermostated compartment of the spectrophotometer at 25 °C. The reaction was initiated by injecting a known amount of olefin with the aid of a glass microsyringe. The addition was accompanied by a vigorous shaking of the cuvette. The kinetics were followed either by the quenching with iodide, as described previously,[38] or by the spectral change monitored at a fixed wavelength. The latter method was applied to fast reactions [e.g., $Hg(OAc)_2$ with 1-pentene, 1-hexene, 1-octene, cyclohexene, cycloheptene, and 2-methyl-2-butene] by following the disappearance of the absorbance at 265 nm in methanol. Since the absorbance at 265 nm which is mainly due to $Hg(OAc)_2$ did not finally reach zero, because of the absorbance from the products, the concentration of $Hg(OAc)_2$ was evaluated by the expression $[Hg(OAc)_2] = [Hg(OAc)_2]_0(A - A_\infty)/(A_0 - A_\infty)$, where A_0 and A_∞ are the initial and the final absorbance, respectively. The quenching method was also applied to the other oxymercuration reactions. Aliquots of the reaction mixture (20 μL) were withdrawn periodically and quickly added to another 10-mm quartz cuvette containing 2.5×10^{-3} M potassium iodide in aqueous methanol of such a composition that the final solution had a mol fraction of 0.91 for MeOH. By this procedure, the mercury(II) derivatives used in this study were all quantitatively converted to triiodomercurate(II), HgI_3^-, instantaneously.[38] Following this, the concentration of the Hg(II) derivatives during the reaction was determined from the absorbance of HgI_3^- at 301.5 nm by using the calibrated equation developed by Abraham and Johnston.[41] The consistency of the two methods was checked with the reactions of $Hg(OAc)_2$ with *cis*-cyclooctene, 2-methyl-2-butene, 4,4-dimethyl-2-pentene, and 3,3-dimethyl-1-butene in methanol. The two methods gave essentially the same results as shown in Figure 5.

The relative reactivities of olefins obtained from the two different direct measurements in this study agreed with those reported in the literature,[11,13a,36] satisfactorily to within ±0.3 in log *k*. For example, the largest difference in the reactivity of olefins, overlapping with our study, is reported at −3.38 in log k^{13a} between cyclooctene and 1-octene, which agrees with −3.58 from our data in Table II. However, some of the absolute rate constants determined in this study differ somewhat from those cited in the literature [e.g., for $t\text{-BuCH}{=}CH_2$, *k* is 0.16 (this study) and 0.50 $M^{-1}\ s^{-1}$ (ref 11)]. The latter were obtained by measuring the decay of the $Hg(OAc)_2$ absorbance. The rate constants obtained by this method are highly sensitive to the final absorbance, particularly of the products mentioned above.

Inhibition of the Photochemical Bromination. Aliquots of a bromine solution (3.0 mL, 1.18×10^{-2} M) in carbon tetrachloride were added to three Pyrex tubes. One tube contained either isoamyl nitrite or galvinoxyl as an inhibitor, and the other was wrapped completely with aluminum foil to compare the photochemical reaction with the thermal reaction. The same amount of 1-hexene (2.66×10^{-2} M) was added to each tube, which was irradiated in a precision merry-go-round apparatus[42] with use of a 100-W incandescent light bulb. The irradiation was periodically interrupted (every 10 min), and the change in bromine concentration was determined spectroscopically. As shown in Figure 10, both inhibitors decreased the photochemical rate. Isoamyl nitrite appeared to be more effective than galvinoxyl. An increase in the concentration of the inhibitors (2.0×10^{-3} to 4.9×10^{-3} M for isoamyl nitrite and 2.6×10^{-5} to 1.7×10^{-4} M for galvinoxyl) did not change the efficiency of inhibition significantly.

Effect of Inhibitors on the Bromination of Olefins. The effect of inhibitors on the bromination of olefins was examined for 1-pentene, 1-hexene, 1-octene, and 2,3-dimethyl-2-butene in carbon tetrachloride. Addition of the same amount of isoamyl nitrite (4.9×10^{-3} M) which was effective in inhibiting the photochemical reaction of 1-hexene and bromine (vide supra) did not change the thermal bromination of the olefins as shown in Figure 4b.

Electron Affinity of Mercury(II) Derivatives. The electron affinities of mercury(II) derivatives listed in Table III were evaluated by Briegleb's method[43] with the use of the expression $E_A(HgX_2) = E_A(Br_2) - [h\nu_{CT}(HgX_2) - h\nu_{CT}(Br_2)]$, where $h\nu_{CT}(HgX_2)$ and $h\nu_{CT}(Br_2)$ are the CT transition energies for the hexamethylbenzene complexes with HgX_2 and Br_2, respectively. The value of $h\nu_{CT}(Br_2)$ is 3.36 eV, and those for $h\nu_{CT}(HgX_2)$ are from ref 22. The value for the electron affinity of Br_2 is 1.48 eV.[33,43] The values of $E_A(HgX_2)$ obtained in this manner are only reliable for the comparative procedure and should not be taken as absolute values.

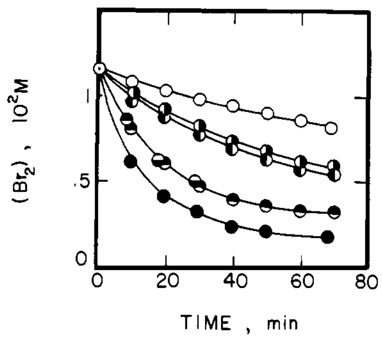


Figure 10. Efficiency of inhibitors on the photochemical reactions of 1.1 × 10^{-2} M Br_2 with 2.7 × 10^{-2} M 1-hexene in CCl_4 at 25 °C under thermal (○) conditions; same as above, but under photochemical irradiation (**I** = 2.7 × 10^{-9} einstein $L^{-1}\ s^{-1}$) with no inhibitor (●), containing isoamyl nitrile [4.9 × 10^{-3} M (◑), 2.0 × 10^{-3} M (◐)] and containing galvinoxyl [2.6 × 10^{-5} M (◓), 1.7 × 10^{-4} M (◒)].

Significance of the Charge-Transfer Formulation in Electrophilic Additions to Olefins. According to the well-established charge-transfer theory developed by Mulliken,[19] the spectral transition $h\nu_{CT}$ represents an electronic excitation from the ground state of the complex to the excited state in the gas phase. For weak complexes of the type described here between olefins and various electrophiles E, this transition corresponds to the process,[44]

$$[{>}C{=}C{<}\ E] \xrightarrow{h\nu_{CT}} [{>}C{=}C{<}^{+}E^{-}]^{*} \qquad (9)$$

where the asterisk identifies an excited ion pair with the same mean separation r_{DA} as that in the EDA complex; i.e., eq 9 represents a vertical (Franck–Condon) transition, the energy of which is given by

$$h\nu_{CT} = I_D - E_A + \omega \qquad (10)$$

where $h\nu_{CT}$, I_D, and E_A were defined earlier. The interaction energy ω of the excited ion pair includes the electrostatic work term ($-e^2/r_{DA}$), the resonance interaction, etc., and varies in a series of olefins as a result of the change in the steric effect. Thus it follows from eq 10 that the energy change, $\Delta E = \omega - \omega_0$ is given by eq 7.[45] The relationships among the charge-transfer transition energy ($\Delta h\nu_{CT}$), the steric term (ΔE), and the energetics of the redox processes for the donor (ΔI_D), as given in eq 7, are schematically represented in the thermochemical cycle **A**.[46] (Note:

$$\begin{tikzcd}
 & {[C{=}C^{+}E^{-}]^{*}} \arrow[dr, "\Delta E"] & \\
(C{=}C\ E) \arrow[ur, "\Delta h\nu_{CT}"] \arrow[rr, "\Delta I_D"] & & C{=}C^{+} + E^{-}
\end{tikzcd}$$

A

the electron affinity E_A of the electrophile is cancelled out.) With use of the same comparative procedure, the relative activation free energy for electrophilic addition is expressed as

$$\log (k/k_0) = -\Delta G_r^{\ddagger}/2.3RT \qquad (11)$$

where the subscript r emphasizes that all energy changes are evaluated relative to the reference olefin, 1-pentene. The thermal path for electrophilic addition is then related to the CT transition in cycle **A** by a

---

[40] Pincock, J. A.; Yates, K. *Can. J. Chem.* **1970**, *48*, 2944.

[41] Abraham, M. H.; Johnston, G. F. *J. Chem. Soc. A* **1970**, 188.

[42] See: Ratcliff, M. A., Jr.; Kochi, J. K. *J. Org. Chem.* **1971**, *36*, 100.

[43] Briegleb, G., *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 617.

[44] (a) The excited states of the EDA complexes (DA) have been proved to be the ion pair (D^+A^-) for various systems by using laser spectroscopy. (b) Nagakura, S. *Excited States* **1975**, *2*, 321 and references cited therein.

[45] For other discussions of ΔE see: Fukuzumi, S.; Kochi, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 2141.

[46] (a) It must be emphasized that this treatment does not depend on whether it can be proved that the EDA complex is, or is not, an intermediate along the reaction pathway. This important point is elaborated in ref 45.

second thermochemical cycle B, in which the difference between the CT

$$\begin{tikzcd} & \left[C{=}C^+E^-\right]^* \arrow[dd, "S"] \\ (C{=}C\ \ E) \arrow[ur, "\Delta h\nu_{CT}"] \arrow[dr, "\Delta G_r^\ddagger"'] & \\ & [\ddagger] \end{tikzcd}$$

B

excited state $[{>}C{=}C{<}^+E^-]^*$ and the transition state $[\ddagger]$ for electrophilic addition is labelled as S. We find that $S = \Delta G_r^\ddagger - \Delta h\nu_{CT}$ for bromination is the same as that for oxymercuration, i.e.,

$$(\Delta G_r^\ddagger - \Delta h\nu_{CT})_{Br_2} = (\Delta G_r^\ddagger - \Delta h\nu_{CT})_{HgX_2} \qquad (12)$$

In other words, *path S is independent of the electrophile.* Such a situation would arise if the representation of the transition state were akin to the thermal ion pair, i.e., $[\ddagger] = [{>}C{=}C{<}^+E^-]$. Under these circumstances the contribution from the electrophile would be minimal, if at all, owing to its cancellation in the comparative procedure. (We showed in a recent study[37] with alkylmetal donors that path S actually corresponds to a solvation change in the donor moiety as it proceeds from the excited ion pair to the thermal ion pair.)

The correlation with the CT transition energies in eq 12 is, in fact, equivalent to the correlation presented with the steric terms in eq 8 since it follows from eq 7 that $(\Delta h\nu_{CT})_{Br_2} - (\Delta h\nu_{CT})_{HgX_2} = \Delta E_{Br_2} - \Delta E_{HgX_2}$ for the same series of olefins with ΔI_D in common. Furthermore, the linear relationship observed in Figure 7 for the various electrophiles accords with the formulation in cycle B since the steric effect induced on a given olefin is not highly dependent on the electrophile.[47]

Acknowledgment. We wish to thank the National Science Foundation for financial support.

Supplementary Material Available: Tables of the effects of bromine and olefin concentrations on the observed third-order rate constants for bromination in CCl_4 (Table IS) and spectral data for the EDA complexes of olefins with Br_2, $HgCl_2$, and $Hg(OAc)_2$ (Table IIS) (3 pages). Ordering information is given on any current masthead page.

---

(47) With use of the comparative method, the change in the interaction energy with a series of electrophiles acting on a *fixed* olefin is given by $\Delta E = \Delta h\nu_{CT} + \Delta E_A$, owing to the cancellation of I_D from eq 10. Accordingly, the steric term for Br_2 relative to $Hg(OAc)_2$ is $[(4.10 - 4.84) + (1.48 - 0.71)]/(2.3RT) = 0.5$, as evaluated for 4,4-dimethyl-2-pentene by using the data in Tables I and III. Thus, the difference of 0.5 is negligible compared to the large changes for $\mathscr{E}$ in Table IV.

Gas-Phase Binding Energies and Spectroscopic Properties of NO^+ Charge-Tranfser Complexes

W. D. Reents, Jr., and B. S. Freiser*

Contribution from the Department of Chemistry, Purdue University,
West Lafayette, Indiana 47907. *Received July 2, 1980*

Abstract: The NO^+ affinities (NOA) of 28 bases were determined by using ion cyclotron resonance (ICR) spectrometry. The NOAs are observed to correlate with the proton affinities (PA) and the first ionization potentials (IP) of the bases for a specific class of compounds. The linearity with IP suggests that bonding to NO^+ is through the highest filled orbital. The photodissociation spectra of the NO^+ complexes were obtained as well. The NO^+ complexes of benzene, toluene, and mesitylene have λ_{max} at 327 nm and onsets for dissociation at 580 nm. The NO^+ complex of diethyl ether has a λ_{max} at 300 nm and an onset for dissociation at 450 nm. The NO^+ complex of ethanol has a λ_{max} at $\leq$240 nm and an onset for dissociation at 440 nm. The NO^+ complexes of ethyl acetate, acetone, and 3-pentanone have λ_{max} at 265 nm and an onset for dissociation at 580 nm. The NO^+ complexes of benzaldehyde and butyraldehyde have λ_{max} at 300 nm and an onset for dissociation at 460 nm. The NO^+ complex of diisopropyl ketone has a λ_{max} at 350 nm and an onset for dissociation at 580 nm. All these spectra exhibit a broad absorption band which is characteristic of charge-transfer complexes. It is evident that the spectra are nearly identical within a class of compounds. The similarity in the spectra for the NO^+ complexes of benzaldehyde and butyraldehyde indicates that NO^+ binds to the carbonyl group in benzaldehyde rather than the aromatic ring. When the site of charge changes from NO (as with 3-pentanone) to the base (as with diisopropyl ketone), the spectrum is altered considerably. Thus the site of charge in the complex may be determined by the photodissociation technique.

Interactions of ions and neutrals in solution have been of great interest for many years. With the advent of mass spectroscopic techniques, gas-phase studies of ion-neutral interactions have yielded a vast quantity of thermodynamic data as well as information on solvation of ions. These studies include the bonding of metal ions to bases (e.g., Cu^+,[1] Ag^+,[1b,d] Fe^+,[2] Ni^+,[2d] Co^+,[2a,d,3] Al^+,[3,4] Mn^+,[3] Cr^+,[3] Ti^+,[3] Si^+,[5a] SiH^+,[5a] SiH_3^+,[5] $Si(CH)_3^+$,[6] $CpNi^+$,[7] CH_3Hg^+,[8] $TiCl_3^+$,[9] $SiCl_3^+$,[9b] and alkali ions[1d,10]) as well as the

---

(1) (a) Burnier, R. C.; Carlin, T. J.; Reents, W. D., Jr.; Cody, R. B.; Lengel, R. K.; Freiser, B. S. *J. Am. Chem. Soc.* **1979**, *101*, 7127–7129. (b) Cody, R. B.; Burnier, R. C.; Reents, W. D., Jr.; Carlin, T. J.; McCrery, D. A.; Lengel, R. K.; Freiser, B. S. *Int. J. Mass Spectrom. Ion Phys.* **1980**, *33*, 37–43. (c) Burnier, R. C.; Byrd, G. D.; Freiser, B. S. *Anal. Chem.* **1980**, *52*, 1641–1650. (d) Castleman, A. W., Jr.; Holland, P. M.; Mark, T. D.; Peterson, K. I.; Keesee, R. G.; Lee, N. "Proceedings of the 28th Annual Conference on Mass Spectrometry Allied Topics"; New York, 1980; pp 68–69. (e) Jones, R. W.; Staley, R. H. *Ibid.* pp 237–238.

(2) (a) Allison, J.; Ridge, D. P. *J. Organomet. Chem.* **1975**, *99*, C11–C14. (b) Foster, M. S.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1975**, *97*, 4808–4814. (c) Dietz, T. G.; Chatellier, D. S.; Ridge, D. P. *J. Am. Chem. Soc.* **1978**, *100*, 4905–4907. (d) Allison, J.; Ridge, D. P. *J. Am. Chem. Soc.* **1979**, *101*, 4998–5009.

(3) Kappes, M. M.; Uppal, J. S.; Staley, R. H. "Proceedings of the 28th Annual Conference on Mass Spectrometry Allied Topics"; New York, 1980; pp 239–240.

(4) Hodges, R. V.; Armentrout, P. B.; Beauchamp, J. L. *Int. J. Mass Spectrom. Ion Phys.* **1979**, *29*, 375–390.

(5) (a) Allen, W. N.; Lampe, F. W. *J. Am. Chem. Soc.* **1977**, *99*, 2943–2948. (b) Allen, W. N.; Lampe, F. W. *J. Am. Chem. Soc.* **1977**, *99*, 6816–6822.

(6) Blair, I. A.; Bowie, J. H. *Aust. J. Chem.* **1979**, *32*, 1389–1393.

0002-7863/81/1503-2791$01.25/0 © 1981 American Chemical Society