

Polarizability Effects and Dispersion Interactions in Alkene-Br₂ π -Complexes

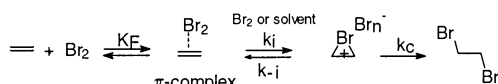
Cinzia Chiappe,^{*,†} Heiner Detert,[‡] Dieter Lenoir,[§] Christian Silvio Pomelli,^{||} and Marie Françoise Ruasse^{*,⊥}

Dipartimento di Chimica Bioorganica e Biofarmacia, Università di Pisa, I-56126 Pisa, Italy, Institut für Organische Chemie, D-55099 Mainz, Germany, Institut für Ökologische Chemie, Postfach 1129, D-85778 Neuherberg bei München, Germany, Dipartimento di Chimica e Chimica Industriale, Università di Pisa, I-56126 Pisa, Italy, and Interfaces, Traitements et Dynamique des Systèmes, Université Paris 7, 75005 Paris, France

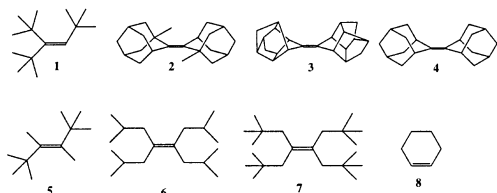
Received July 10, 2002; E-mail: cinziac@farm.unipi.it

Weakly bound molecular complexes,^{1,2} the formation of which is contrary to normal rules of valency,³ play an important role in chemistry, physics, and biodisciplines, like energetics of enzymatic reactions. Charge-transfer (CTC) or electron donor–acceptor (EDA) complexes have been postulated in many common organic reactions,³ although evidence for their involvement on the reaction coordinate is generally weak. However, in electrophilic aromatic substitutions, the role of the preorganization of the reagents within these complexes has been stressed recently by Kochi:^{3c,d} “...the preorganization... can lead to a determined viable transition-state structure, which hitherto may be discounted owing to the high endergonic driving forces”.^{3d}

Electrophilic halogen addition to alkenes is another reaction for which the immediate formation of an olefin-bromine π -complex (“outer” complex)⁴ has been known for a long time.⁵ Recently, it has been shown that 1:1 olefin-Br₂ complexes are essential intermediates in these additions.⁶



Geometry calculations^{7–9} indicated that the charge transfer is very low, in agreement with the rotational spectrum of the ethylene-Br₂ complex in the gas phase.^{8a} This is true for ethylene and similar compounds but is not necessarily true for other olefins. Experimental data on spectral characteristics and association constants for these complexes are scarce, mainly due to the very high rate of their subsequent ionization. For π -complexes between bromine and simple linear alkenes, a linear correlation between $h\nu_{CTC}$ and the donor ionization potential, IP, has been found,⁵ in accordance with the usual Mulliken theory.^{3,4} Herein, we report the first evidence of a direct relationship between association constants, K_F , of the π -complexes and polarizability of the olefins, whereas the expected



parallel trend between $h\nu_{CTC}$ or $\log K_F$ and IP is not observed for the considered set of olefins.

The UV spectral data and K_F values of the π -complexes of alkenes **1–8** and Br₂, determined in this work and previously by our group, are listed in Table 1.

[†] Dipartimento di Chimica Bioorganica e Biofarmacia, Università di Pisa.

[‡] Institut für Organische Chemie.

[§] Institut für Ökologische Chemie.

^{||} Dipartimento di Chimica e Chimica Industriale, Università di Pisa.

[⊥] Université Paris.

Table 1. Calculated and Experimental Parameters Related to Several Alkenes and Bromine π -Complexes in DCE

	CEP-121G (d,p)				6-311+G**				ref	
	α_a	α au	IP ^a eV	d_6 au	α au	IP ^a eV	K_F^b M ⁻¹	λ_{max} nm		ϵ_{max}
1	-2.28	169.7	7.95	1286.6	172.3	8.09	147	270	2350	
2	-2.88	240.2	7.27	1727.7	242.0	7.38	1850	270	9700	6h
3	-2.88	228.3	7.48	1672.4	229.5	7.64	768	267	9100	6c
4	-2.58	214.0	7.37	1554.8	219.4	7.51	289	272	18 000	6g
5	-2.18	145.5	7.76	1086.9	147.5	7.88	84	272	23 000	6d
6	-2.44	201.5	7.16	1436.8	221.2	7.27	9.71	260	4960	6b
7	-2.68	266.1	7.43	1940.5	274.7	7.08	1.6	272	48 000	6f
8	-0.96	67.7	8.79	542.8	69.5	8.95	0.47	287	5500	6a
9	-0.61	72.6	9.35	601.8	74.5	9.51	0.33 ^c	270 ^d		14
10	-0.57	72.1	9.30	595.8	74.2	9.45	0.15 ^c			14

^a In agreement with the experimental or previously calculated (refs 10b, 3c, 11) IPs, for example, **4** IP_{exp} = 7.76 eV; **4** IP_{calc} = 7.49 eV; **8** IP_{exp} = 8.94 eV; **9** IP_{exp} = 9.48 eV. ^b At 25 °C. ^c In CCl₄. ^d In Freon 113 (ref 5).

With the exception of **4**,^{10,3c} and **9**,¹¹ the IP values for the considered olefins have not been measured but can be calculated. Calculations have been performed initially at the B3LYP/CEP-121G (d,p) level (see Supporting Information). The molecular geometry was optimized, and the IP values were computed as the difference between the electronic energy of the neutral olefin and that of the radical cation at the same geometry (vertical ionization energy).^{10b} At the same geometry, the IP values were also calculated at the B3LYP/6-311+ (d,p) level. No satisfactory correlation has been, however, found between K_F and the calculated IP values.

To analyze the substituent effects on K_F , we have first used the Taft–Topsom equation.¹² This model has been recently applied¹³ with success to some thiocarbonyl-I₂ complexes.

If we exclude the two tetrasubstituted alkenes bearing flexible alkyl chains (**6** and **7**), able to shield the double bond to Br₂ approach,^{10c} the K_F values, including those previously reported¹⁴ for **9** and **10** (**9**, 1-hexene; **10**, 4-methyl-pent-1-ene) in CCl₄, are fairly well correlated ($r = 0.995$) with α_a , the polarizability constants of the substituents¹² (Figure 1) with a negative slope ($\rho_\alpha = -1.65 \pm 0.06$). To evaluate more accurately the polarizability, (α), that is, the aptitude of the electronic cloud to undergo deformation under the action of an electric field, we performed ab initio calculations on the olefins **1–10** at the B3LYP/CEP-121G (d,p) and B3LYP/6-311+ (d,p) level. Very similar values were found at both levels.¹⁵

On the basis of the computed α and IP for alkene and Br₂, the strength of the induced dipole–induced dipole dispersion interactions (d_6 , atomic units) has been therefore calculated:

$$d_6 = \frac{3}{2} \alpha_1 \alpha_2 \frac{IP_1 IP_2}{IP_1 + IP_2} \quad (1)$$

with indexes 1 and 2 for bromine ($\alpha_1 = 30.35$ au, IP₁ = 0.387 eV) and olefin, respectively. Again, with the exception of **6** and **7**, fairly

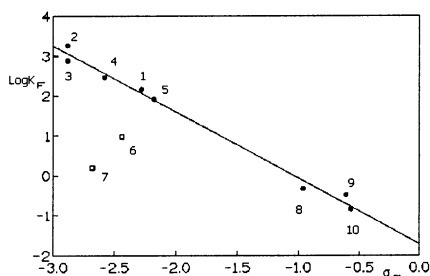


Figure 1. Correlation between K_F and σ_α .

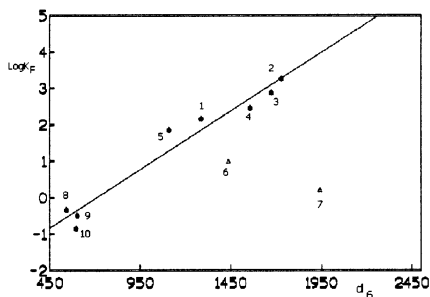


Figure 2. Correlation between $\log K_F$ and d_6 .

good correlations were obtained when $\log K_F$ values were plotted versus computed α or d_6 values ($r = 0.970$ and 0.973),^{10c,16} Figure 2.

These correlations strongly suggest that interactions different from the dispersion ones (e.g. steric interactions, molecular motions, charge transfer, and/or inductive effects) vary little from one system to another. It is noteworthy that for crowded alkenes 1–5, the term in IP of eq 1 does not vary significantly, and α is the dominant term, whereas the opposite is observed for 8–10. Equation 1 is therefore more general than the usual Mulliken analysis and is able to account for the substituent effects of both linear and caged alkenes.

In agreement with the nonexclusive role of IP on the stability of these π -complexes is also the extremely low, if any, variation in the complex absorption maximum (λ_{\max}).¹⁷ Furthermore, the value of λ_{\max} for the cyclohexene- Br_2 complex shows a surprising red shift with respect to the tetrasubstituted olefins.¹⁷ Although, at least for planar complexes, the separation d between donor and acceptor ($d = e^2/w$), may affect the absorption maximum, B3LYP calculations seem to exclude this latter hypothesis.¹⁶ Deviations from the linear (Mulliken) correlation are, however, not necessarily exceptional and can suggest a variation in the inner/outer character^{3a,c} of the complex on going from linear to caged alkenes.

Finally, we want to underline that the ρ_α value found here can be used to estimate the contribution of the substituent effects on K_F to the overall value of ρ_{exp} ($k_{\text{exp}} = K_F k_i k_c / (k_{-i} + k_c)$). Because kinetic data for bromination of simple ethenes suggest¹⁸ that the reactivity ratios of these olefins are scarcely affected by the solvent, and only a modest solvent effect has been observed on K_F ,^{6b} we can evaluate that the polarizability effects on K_F contribute approximately to 75% of the overall change in rate due to changes in alkene structure, $\rho_{\alpha(\text{exp})} = -2.15$.¹⁹ It is noteworthy that in the addition of ICl to alkenes, an irreversible reaction, the substituent effects on the 1:1 ICl -alkene complexes contribute to the overall change in rate by ca. 24%.²⁰ This may suggest a more important return in olefin bromination or a charge development in the π -complexes of caged alkenes larger than those of linear alkenes. In olefin 4, the calculated distances between the two homoallylic protons, which are directed toward Br_2 , are 4.51, 5.08, and 5.32 Å in the unsubstituted olefin, π -complex, and bromonium ion, respectively. At variance with ethylene for which practically no rehybridization has been calculated on going from olefin to the

complex, in 4 a significant rehybridization at the carbon occurs already in the π -complex, suggesting an “inner” character more important than that in complexes of linear alkenes. In conclusion, the present data reveal that the stability of the Br_2 -olefin π -complexes is affected by both the donor ionization potential and the polarizability of the $\text{C}=\text{C}$ bond. Equation 1, taking into account both effects, is able to describe these transient species better than the Mulliken analysis. Furthermore, the comparison of the data suggests that the magnitude of the charge transfer within these complexes depends significantly on the polarizability of the olefins.

Acknowledgment. The authors thank Prof. J. L. M. Abboud for valuable comments.

Supporting Information Available: Optimized geometries (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) Benesi, H. A.; Hildebrand, J. H. *J. Am. Chem. Soc.* **1949**, *71*, 2703.
- (2) (a) van der Waals Complexes.III. *Chem. Rev. Special Thematic Issue* **2000**, *100*. (b) Warshel, A. *Theor. Chem. Acc.* **2000**, *103*, 307.
- (3) (a) Forster, T. *Organic Charge-Transfer Complexes*; Academic Press: London and New York, 1969. (b) Andrews, L. J.; Keefer, R. M. *Molecular Complexes in Organic Chemistry*; Holden-day: San Francisco, 1964. (c) Rathore, R.; Kochi, J. K. *Adv. Phys. Org. Chem.* **2000**, *35*, 193. (d) Rosokha, S. V.; Kochi, J. K. *J. Org. Chem.* **2002**, *67*, 1727.
- (4) Mulliken distinguishes “outer complexes” with small charge transfer between donor and acceptor and “inner complexes” with extensive charge redistribution. Mulliken, R. S.; Person, W. B. *Molecular Complexes*; Wiley-Interscience: New York, 1969.
- (5) Dubois, J.-E.; Garnier, F. *Spectrochim. Acta, Part A* **1967**, *23*, 2288.
- (6) (a) Bellucci, G.; Bianchini, R.; Ambrosetti, R. *J. Am. Chem. Soc.* **1985**, *107*, 2464. (b) Brown, R. S.; Slebocka-Tilk, H.; Bellucci, G.; Bianchini, R.; Ambrosetti, R. *J. Am. Chem. Soc.* **1990**, *112*, 6310. (c) Bellucci, G.; Bianchini, R.; Chiappe, C.; Gadgil, V. R.; Marchand, A. P. *J. Org. Chem.* **1993**, *58*, 3575. (d) Bellucci, G.; Bianchini, R.; Chiappe, C.; Lenoir, D.; Attar, A. *J. Am. Chem. Soc.* **1995**, *117*, 6243. (e) Bellucci, G.; Chiappe, C.; Bianchini, R.; Lenoir, D.; Herges, R. *J. Am. Chem. Soc.* **1995**, *117*, 12001. (f) Bianchini, R.; Chiappe, C.; Lenoir, D.; Lemmen, P.; Herges, R.; Grunenberg, J. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1284. (g) Bellucci, G.; Bianchini, R.; Chiappe, C.; Marioni, F.; Ambrosetti, R.; Brown, R. S.; Slebocka-Tilk, H. *J. Am. Chem. Soc.* **1989**, *111*, 2640. (h) Chiappe, C.; De Rubertis, A.; Lemmen, P.; Lenoir, D. *J. Org. Chem.* **2000**, *65*, 1273.
- (7) Prinsette, J.; Seger, G.; Kochanski, E. *J. Am. Chem. Soc.* **1978**, *100*, 6941.
- (8) (a) Legon, A. C.; Thumwood, J. M. A. *Phys. Chem. Chem. Phys.* **2001**, *3*, 1397. (b) Chiappe, C.; De Rubertis, A.; Detert, H.; Lenoir, D.; Schleyer, P. v. R.; Wannere, C. S. *Chem.-Eur. J.* **2002**, *8*, 967.
- (9) Legon, A. C. *Angew. Chem., Int. Ed.* **1999**, *38*, 2686.
- (10) (a) Nelsen, S. F.; Klein, S. J.; Triber, D. A., II; Ismagilov, R. F.; Powell, D. R. *J. Org. Chem.* **1997**, *62*, 6539. (b) Nelsen, S. F.; Reinhardt, L. A. *J. Phys. Org. Chem.* **2001**, *14*, 847. (c) σ_α and α are linearly related to n_{eff} , “effective number of carbons in the alkyl substituents”. In a $\log K_F/n_{\text{eff}}$ correlation, analogous to that in Figure 2, 6 and 7 are also not included. Correlations in Figures 1 and 2 with σ_α and d_6 are markedly better than that with n_{eff} .
- (11) Masclat, P.; Grosjean, D.; Mouvier, G.; Dubois, J. E. *J. Electron. Relat. Phenom.* **1973**, *2*, 225.
- (12) Taft, R. W.; Topsom, R. D. *Prog. Phys. Org. Chem.* **1987**, *16*, 1.
- (13) Essefar, M.; Bouab, W.; Lamsabhi, A.; Abboud, J.-L. M.; Notario, R.; Yáñez, M. *J. Am. Chem. Soc.* **2000**, *122*, 2300.
- (14) (a) Sergeev, G. B.; Serguchev, Yu. A.; Smirnov, V. V. *Russ. Chem. Rev.* **1973**, *697*. (b) Sergeev, G. B.; Smirnov, V. V.; Bakarinova, G. A. *Vestn. Mosk. Univ. Khim.* **1974**, *15*, 358.
- (15) (a) Cammi, C.; Mennucci, B.; Tomasi, J. *J. Phys. Chem. A* **2000**, *104*, 4690. (b) α can also be obtained experimentally by refraction index measurements. Butcher, P. N.; Cotter, D. *The Elements of Nonlinear Optics*; Cambridge University Press: Cambridge, 1990.
- (16) The correlation is slightly better using E_d , the interaction energy ($E_d = d_6/r^6$), instead of d_6 alone, with r_{calcd} for 8 and 4 and interpolated values for the other complexes. r , the calculated Br_2 -double bond distance in the complex, is 2.81 and 2.41 Å for 8 and 4, respectively.
- (17) For weak CTC, the UV absorption generally occurs with $hc/\lambda_{\max} = I - E - w$, where I is the ionization energy of the donor, E is the electron affinity of the acceptor, and w is the electrostatic energy of the ion pair $[\text{D}^+\text{A}^-]$.
- (18) Ruasse, M. F.; Argile, A.; Bienvenue-Goët, E.; Dubois, J.-E. *J. Org. Chem.* **1979**, *44*, 2758. Ruasse, M. F.; Zhang, B. L. *J. Org. Chem.* **1984**, *49*, 3207.
- (19) Because there is a good relationship between σ^* and σ_α for alkyl groups with a slope of 1.44, the usual relationship ($\log(k/k_0) = -3.1\sigma^*$) for bromination of alkyl substituted olefins in methanol becomes $\log(k/k_0) = -2.15\sigma_\alpha$.
- (20) Schmid, G. H.; Gordon, J. W. *Can. J. Chem.* **1986**, *64*, 2.

JA027630G