Weakly bound molecular complexes, the formation of which is contrary to normal rules of valency, play an important role in chemistry, physics, and biodynamics, like energetics of enzymatic reactions. Charge-transfer (CTC) or electron donor–acceptor (EDA) complexes have been postulated in many common organic reactions, 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: ...the preorganization... can lead to a determined viable transition-state structure, which hitherto may be discounted owing to the high endergonic driving forces.

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

Geometry calculations indicated that the charge transfer is very low, in agreement with the rotational spectrum of the ethylene-Br₂ complex in the gas phase. 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 hvCTC and the donor ionization potential, IP, has been found, in accordance with the usual Mulliken theory. Herein, we report the first evidence of a direct relationship between association constants, KF, of the π-complexes and polarizability of the olefins, whereas the expected parallel trend between hvCTC or log KF and IP is not observed for the considered set of olefins.

The UV spectral data and KF 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.

| Table 1. Calculated and Experimental Parameters Related to Several Alkenes and Bromine π-Complexes in DCE |
|---|---|---|---|---|---|---|
| Alkene | hvCTC | KF | α | IP | KF | νmax |
|---|---|---|---|---|---|
| 1 1-butene | 169.7 | 7.95 | 2.44 | 141.5 | 6.14 | 377 |
| 2 1-hexene | 240.2 | 7.27 | 221.2 | 7.27 | 260 | 4960 |
| 3 2-octene | 228.3 | 7.16 | 212.2 | 7.16 | 260 | 4960 |
| 4 2-methyl-pent-1-ene | 214.0 | 7.37 | 219.4 | 7.37 | 242.0 | 7.16 |
| 5 4-methyl-pent-1-ene | 145.7 | 7.16 | 147.5 | 7.16 | 272 | 18000 |
| 6 2-bromo-1-octene | 101.5 | 7.16 | 101.5 | 7.16 | 272 | 18000 |
| 7 2,3-dimethylpent-1-ene | 143.8 | 7.16 | 147.5 | 7.16 | 272 | 18000 |
| 8 4-bromo-1-pentene | 172.7 | 7.16 | 172.7 | 7.16 | 272 | 18000 |

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

These correlations strongly suggest that interactions differ 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 $\alpha$ 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 $\pi$-complexes is also the extremely low, if any, variation in the complex absorption maximum ($\lambda_{\text{max}}$).$^{11}$ Furthermore, the value of $\lambda_{\text{max}}$ for the cyclohexene-BF$_2$ 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 ($d = c^2/n^2e$), may affect the absorption maximum. B3LYP calculations seem to exclude this latter hypothesis.$^{18}$ Deviations from the linear (Mulliken) correlation are, however, not necessarily exceptional and can suggest a variation in the inner/outer character$^{19,20}$ of the complex on going from linear to caged alkenes.

Finally, we want to underline that the $\rho_0$ value found here can be used to estimate the contribution of the substituent effects on $K_F$ to the overall value of $\rho_{\text{esp}}$ ($k_{\text{esp}} = K_Fk_D/k_+ + k_-)$). Because kinetic data for bromination of simple ethenes suggest$^{18}$ 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 alkenes, but not in ICI to alkenes, an irreversible reaction, the substituent effects on the 1:1 ICI-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 $\pi$-complexes of caged alkenes rather than those of linear alkenes. In olefin 4, the calculated distances between the two homoallylic protons, which are directed toward BF$_2$, are 4.51, 5.08, and 5.32 Å in the unsubstituted olefin, $\pi$-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 $\pi$-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 $\pi$-complexes is affected by both the donor ionization potential and the polarizability of the C=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.

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

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(10) (a) Nielsen, S. F.; Klein, C. J.; Tribet, D. A.; H.; Isakoff, R. F.; Powell D. R. J. Org. Chem. 1997, 62, 6539. (b) Nielsen, S. F.; Reinhardt, L. A. J. Phys. Org. Chem. 2001, 14, 847. (c) $\alpha$ and $\alpha$ are linearly related to $n_0$, “effective number of carbons in the alkyl substituents”. In a log $K_F$ vs $n_0$ correlation, analogous to that in Figure 2 and 7 are also not included. Correlations in Figures 1 and 2 with $\alpha$ and $\alpha$ are markedly better than that with $n_0$.
(16) The correlation is slightly better using $E_\alpha$, the interaction energy ($E_\alpha = E\alpha$), instead of $d_6$ alone, with $r_{\text{d}}$ and $r_{\text{i}}$ and interpolated values for the other complexes, 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 $h\lambda_{\text{max}} = 1 - E / w$, where $E$ is the ionization energy of the acceptor, and $w$ is the electrostatic energy of the ion pair $D^+ A^-$. E$^+$1.
(19) Because there is a good relationship between $\theta_0$ and $\alpha$ for alkyl groups with a slope of 1.44, the usual relationship (log($K_F$) = $-3.1\theta_0$) for bromination of alkyl substituted olefins becomes log($K_F$) = $-2.15\alpha$.

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