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Large Formation Constant of a Transient 1:1 *dl*-D_3-Trishomocubylidene-D_3-trishomocubane·Br_2 Charge-Transfer Complex: General Implications for the Mechanism of Electrophilic Bromination of Olefins

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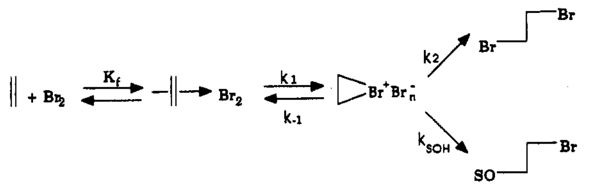
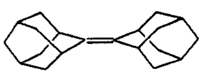
Olefin–Br_2 charge-transfer complexes (CTC) have been shown[1,2] to be the precursors of the bromonium–bromide or polybromide ($n = 3, 5$)[3,4] ion pair intermediates involved in the ionic bromination of olefins (eq 1). It has been recognized[4,5] that this preequilibrium tends to reduce the information content of the k_{obsd} for bromination, unless structural effects on K_f, k_{-1}, and k_2 (or k_{SOH}) are much smaller than those on k_1. The following recent data show, however, that alkyl substitution on the double bond as well as substituent steric effects have a very large influence on K_f: in 1,2-dichloroethane at 25 °C $K_f = 0.47$ M^{-1} for cyclohexene,[2] 9.71 M^{-1} for tetraisobutylethylene,[6] and 2.89×10^2 M^{-1} for adamantylideneadamantane (1).[4] The comparison with the last compound was, however, subjected to criticism,[7] because 1 is an atypical olefin in that its bromination does not lead to the normal addition product but stops at the stage of bromonium ion formation.[4] In this paper we are reporting on the determination of K_f of a 1:1 CTC between Br_2 and *dl*-D_3-trishomocubylidene-D_3-trishomocubane (2), a tetrasubstituted "cage" olefin similar to 1, which, however, does react with Br_2 to give the expected 1,2-dibromide 3. The results confirm a large increase in K_f with increasing substitution on the double bond.



(1)

Equal volumes of a 3.2×10^{-4} M solution of Br_2 and of 3.2×10^{-4} to 1.5×10^{-2} M solutions of 2[8] in 1,2-dichloroethane were mixed at 25 °C in a stopped-flow apparatus, and the reactions were monitored in a wavelength range between 250 and 350 nm. Initial absorbances, which were measured immediately after the reactants had been mixed, were significantly higher than those expected on the basis of analytically determined Br_2 concentrations. These measured absorbances were found to increase with increasing concentrations of substrate 2 at constant Br_2 concentration. Figure 1 shows these initial absorbances (A_0) measured at 25 °C and 300 nm, where the Br_2 absorption is near to its minimum ($\epsilon_{300} = 13$ M^{-1} cm^{-1}), as a function of the concentration of 2. The curve is consistent with a progressive complexation of Br_2 by the olefin to give a CTC, saturation being attained at a concentration of 2 above ca. 6×10^{-3} M.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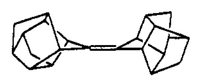
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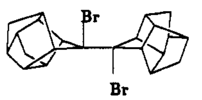

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The data of Figure 1 were fitted to the Scott equation for a 1:1 complexes,[9] ignoring the small contribution to A_0 by free Br_2. A satisfactory fit was obtained, giving $K_f = 7 \times 10^2$ M^{-1} and $\epsilon_{300} = 3.4 \times 10^3$ M^{-1} cm^{-1} for the 1:1 CTC. These estimates were used as starting parameters in a nonlinear least-squares fitting procedure[4] including the entire set of A_0–concentration data obtained in the 250–350-nm range and taking into account the free Br_2 contribution to A_0. This yielded a final value of K_f of 7.68 (0.85) $\times 10^2$ M^{-1} at 25 °C and the molar extinction coefficients of the 1:1 CTC at all examined wavelengths. This K_f is only 2.6 times larger than that found for 1. The root-mean-square residual of the fit was 0.048, and the correlation coefficients between the K_f and any of the ϵ never exceeded ±0.8. The obtainment of a very satisfactory fit to an equation derived for 1:1 complexes excluded any significant contribution to the CTC band by species of 1:2 stoichiometry like a bromonium–tribromide, formed by Br_2-assisted ionization of the CTC, whose Br_3^- counteranion should absorb in the same region. In contrast to the 1–Br_2 system, where the impossibility to proceed beyond the formation of the bromonium–polybromide species allows their equilibrium accumulation, in the case of 2 the collapse to dibromide 3 prevents this accumulation in relevant amounts.

The computed best fit UV spectrum of the 2·Br_2 CTC is shown in Figure 2. The absorption maximum, $\lambda_{max} = 267$ (1) nm ($\epsilon_{max} = 9.1$ (0.7) $\times 10^3$ M^{-1} cm^{-1}), is near to those observed for the analogous tetraisobutylethylene·Br_2 (260 nm)[6] and adamantylideneadamantane·Br_2 CTC (272 nm).[4]

The CT band decayed fast according to the integrated second-order rate law of eq 2, with a k_{obsd}, measured at several wavelengths, of 3.0 (0.5) $\times 10^5$ M^{-1} s^{-1}. The dibromo adduct 3 was the final product.[10] This k_{obsd} cannot simply be the rate constant for the dissociation of the CTC to a bromonium–tribromide ion pair because such dissociation is too fast for the stopped flow time scale in the case of 1 and is expected to be as fast for 2. The k_{obsd} is rather related to the product-forming step, which is retarded, although to a much lower extent than in the case of 1, by

$$1/A_{CT} = 1/A_{0CT} + (k_{obsd}/\epsilon_{CT})t \qquad (2)$$

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[1] Garnier, F.; Donnay, R. H.; Dubois, J. E. *Chem. Commun.* **1971**, 829.

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[7] Reference 5, footnote 17b.

[8] Marchand, A. P.; Reddy, G. M.; Deshpande, M. N.; Watson, W. H.; Nagl, A.; Lee, O. S.; Osawa, E. *J. Am. Chem. Soc.* **1990**, *112*, 3521.

[9] Scott, R. L. *Recl. Trav. Chim, Pays-Bas* **1965**, *75*, 787.

[10] This is at variance with the behavior of *meso*-D_3-trishomocubylidene-D_3-trishomocubane, giving a rearranged spiro compound; see: ref 8. Lee, O. S.; Osawa, E. *Bull. Korean. Chem. Soc.* **1992**, *13*, 59.

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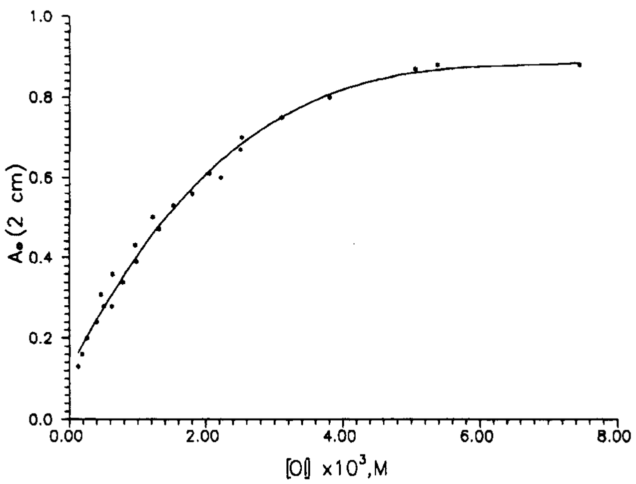

Figure 1. Initial absorbances (A_o) at 300 nm of mixtures of 1.6 × 10^{-4} to 7.5 × 10^{-3} M *dl*-D_3-trishomocubylidene-D_3-trishomocubane and 1.6 × 10^{-4} M Br_2 in 1,2-dichloroethane at 25 °C against the olefin concentrations.

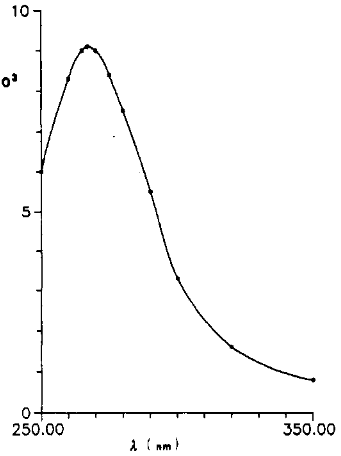

Figure 2. Computed best fit spectrum of the 1:1 *dl*-D_3-trishomocubylidene-D_3-trishomocubane·Br_2 CTC in 1,2-dichloroethane.

steric effects on nucleophilic attack by the counteranion at the bromonium carbons.

The results obtained in the present study for bromination of 2 suggest that the C=C double bond in "cage" olefins such as 1 and 2 is more accessible for Br_2 complexation than in other tetraalkylated olefins which contain branched alkyl groups (e.g., tetraisobutylethylene).[6] The change in hybridization concomitant with bromonium ion formation in 1 and 2 causes the two "cage" moieties in each substrate to approach one another. The proximity of the "cage" moieties in the resulting bromonium ions in each case effectively impedes subsequent backside attack by the counteranion. This deleterious steric effect is more pronounced in the case of bromine addition to 1 than to 2.[11] The K_f of 7.68 × 10^2 M^{-1} found for the 2·Br_2 CTC can therefore be taken as a lowest limiting evaluation for unhindered tetrasubstituted olefins. The comparison of this value with that found for the cyclohexene·Br_2 CTC indicates that in 1,2-dichloroethane the K_f increases at least by a factor of 10^3 on passing from a 1,2-disubstituted to a tetrasubstituted olefin. These data provide therefore a definite confirmation for the previously inferred large dependence of K_f of olefin·Br_2 CTC's on substituent effects.[4] This dependence is likely to be similar in other solvents because solvent effects on K_f are modest.[2,6,12]

It has been assumed that electronic effects of substituents on k_1 are much higher than those on K_f because of the much larger charge development in the TS for the ionization step than in CTC formation.[5] Since in crowded olefins steric effects influence k_{obsd} much more than K_f,[13] a rigorous check of this assumption would require a knowledge of both K_f and k_{obsd} for uncrowded olefins in the same solvent. Unfortunately, this is not possible at present because in solvents like 1,2-dichloroethane tri- and tetrasubstituted uncrowded olefins react so fast that neither k_{obsd} nor K_f are accessible, even using fast kinetic techniques like the stopped flow. Kinetic data for mono- to tetraalkyl-substituted ethylenes have been reported in Freon112,[14] but, having been obtained by poorly performant techniques, they could be not reliable. Kinetic constants have been accurately measured for ethylene to tetramethylethylene in methanol,[15] but again the relative K_f are not experimentally accessible in this solvent because of the too high bromination rates. However, kinetic data for the bromination of ethylene- and methyl-substituted ethylenes show that very similar rate increases for the same changes in substitution occur in solvents as different as methanol or ethanol and acetic acid.[15,16] Thus, the conversion of ethylene to its 1,1-dimethyl and to its *cis*- and *trans*-1,2-dimethyl derivative causes respective rate enhancements in methanol of 8 × 10^3-, 5.1 × 10^3- and 2.8 × 10^3-fold;[15] likewise, the conversion of propene to trimethylethylene gives a rate increase of 3.2 × 10^3-fold in methanol and 3.8 × 10^3-fold in acetic acid,[16] while changing from 1,1-dimethyl-, *cis*-1,2-dimethyl-, and *trans*-1,2-dimethyl-substituted to tetramethyl-substituted ethylene produces respective rate enhancements of 2.9 × 10^2-, 6.1 × 10^2- and 1.1 × 10^3-fold in methanol and 4.6 × 10^2-, 5.7 × 10^2- and 7.5 × 10^2-fold in acetic acid.[16] Similar rate increases of 2.6 × 10^2 and 4.1 × 10^2 have been respectively found on passing from *cis*-2-pentene and *trans*-2-pentene to tetramethylethylene in ethanol.[16]

All these data suggest that the reactivity ratios of these olefins are scarcely affected by the solvent, and therefore they should likely be of the same magnitude in 1,2-dichloroethane, too. On this basis, and on account of the modest solvent effects on K_f, it can be inferred that an increase by two in number of alkyl substituents on the double bond increases both the K_f and the k_{obsd} roughly by a factor of 10^3. This point indicates that substituent effects are not much more influential on k_{obsd} than on K_f. A possible rationalization of the lower accelerating effect by alkyl substituents on the bromination rates, relative to what could be expected for an Ad_EC1 mechanism on the basis of their effects on K_f, could be found in a reversible ionization of CTC's to bromonium–bromide ion pairs. This reversibility, which has been unambiguously demonstrated

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[11] A reviewer has suggested that the lack of dibromide formation from 1 may be due to reversibility of the product-forming step, the covalent dibromide being unstable toward ionization under the reaction conditions. Although this hypothesis cannot be checked experimentally because of the unavailability of this dibromide, it seems to us to be less probable, since the similarly substituted dibromide 3 is stable.

[12] Ruasse, M.-F.; Motallebi, S. *J. Phys. Org. Chem.* **1991**, *4*, 527.

[13] In the limiting case of adamantylideneadamantane K_f is 289 M^{-1}, whereas k_{obsd} is zero.[4]

[14] Garnier, F.; Dubois, J.-E. *Bull. Soc. Chim. Fr.* **1968**, 3797.

[15] Ruasse, M.-F.; Argile, A.; Bienvenue-Goëtz, E.; Dubois, J.-E. *J. Org. Chem.* **1979**, *44*, 2758.

[16] Ruasse, M.-F.; Zhang, B.-L. *J. Org. Chem.* **1984**, *49*, 3207.

by different approaches,[17] should practially result in a decreased ionization rate and therefore in a decrease in the k_{obsd} for bromination.

Experimental Section

dl-D_3-Trishomocubylidene-D_3-trishomocubane (2), was prepared and purified as reported.[8] 1,2-Dichloroethane (Fluka, >99.5%) and bromine (C. Erba RPE >99.5%) were treated as previously described.[18]

1,2-Dichloroethane solutions of 2 and Br_2 were prepared by weighing the reagents in accurately calibrated volumetric flasks. The Br_2 solutions were stored in the dark, checked spectrophotometrically[18] for their concentrations, and discarded when absorptions around the Br_2 UV minimum (280–350 nm) higher than expected were found.

Equal volumes of solutions of 2 and of Br_2, prethermostated at 25 °C, were mixed in a Durrum Model D-110 stopped flow apparatus equipped with a 2-cm observation cell and coupled to a data acquisition system.[2] Absorbances were recorded at several wavelengths between 250 and 350 nm.

For the determination of K_f, the initial absorbances (A_o) at 300 nm were first fit to the Scott equation[9] in order to obtain a preliminary evaluation. The composite A_o data for all runs were then fit by the already described nonlinear least-squares procedure[4,6] that yielded both K_f and the spectrum at the measured wavelengths for the CTC.

The kinetic constants (k_{obsd}) have been obtained by fitting the $A(t)$ values recorded at each wavelength to eq 2, using for ϵ_{CT} the values obtained in the above fitting (see Figure 2). Reproducible values of k_{obsd} were obtained at each wavelength. The k_{obsd} quoted in the text is an average value.

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(17) Bellucci, G.; Bianchini, R.; Chiappe, C.; Brown, R. S.; Slebocka-Tilk, H. *J. Am. Chem. Soc.* 1991, *113*, 8012 and references cited therein.

(18) Bellucci, G.; Berti, G.; Bianchini, R.; Ingrosso, G.; Ambrosetti, R. *J. Am. Chem. Soc.* 1980, *102*, 7480.