A Dynamic NMR Investigation of the Adamantylideneadamantane/Br_2 System. Kinetic and Thermodynamic Evidence for Reversible Formation of the Bromonium Ion/Br_n^- Pairs

G. Bellucci,* R. Bianchini,[†] and C. Chiappe
Dipartimento di Chimica Bioorganica, University of Pisa, 56126 Pisa, Italy

R. Ambrosetti
Istituto di Chimica Quantistica ed Energetica Molecolare del C.N.R., 56126 Pisa, Italy

Donata Catalano
Dipartimento di Chimica e Chimica Industriale, University of Pisa, 56126 Pisa, Italy

A. J. Bennet,[‡] H. Ślebocka-Tilk, G. H. M. Aarts, and R. S. Brown*
Department of Chemistry, University of Alberta, Edmonton, Alberta, T6G 2G2 Canada

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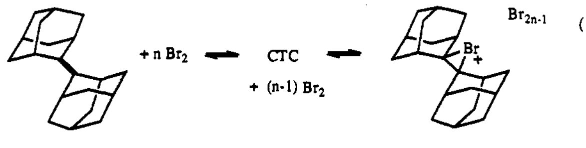
A dynamic ^1H NMR study of the adamantylideneadamantane (Ad=Ad)/Br_2 system has been undertaken in d_4-1,2-dichloroethane as a function of excess [Br_2] and temperature. Bromine site exchange rate constants (k_{NMR}) were determined by line shape analysis of the spectral region between δ 2.1 and 2.6. The temperature range between the fast and slow exchange limits for a given [Br_2] is unusually narrow, being ~15 °C. Increasing [Br_2] at a given temperature dramatically reduces the k_{NMR} due to the equilibrium formation of Br_3^-, Br_5^- and Br_7^-/bromonium ion pairs. It is shown that the dynamic phenomena proceed via the rate-limiting dissociation of a 1:1 charge–transfer complex to free Ad=Ad + Br_2. General implications for the bromination of more reactive olefins are discussed.

Introduction

Adamantylideneadamantane (Ad=Ad) is a unique olefin in that its electrophilic reaction with Br_2 leads to a charge–transfer complex (CTC) and bromonium ion (I-Br^+) that cannot proceed to products (eq 1).[1,2] The



(1)

Ad=Ad (I) (n = 1, 2, 3, ...) (I-Br^+)

bromonium ion tribromide salt (I-Br^+/Br_3^-), as a yellow crystalline material, is sufficiently stable to allow X-ray diffraction studies.[3] However, when dissolved in chlorinated hydrocarbons such as 1,2-dichloroethane (DCE), I-Br^+/Br_3^- was shown to rapidly establish an equilibrium consisting of Ad=Ad, free Br_2, CTC, I-Br^+/Br_3^-, and a fourth partner believed to be I-Br^+/Br_5^-.[4] The establishment of this equilibrium suggests that dynamic NMR (DNMR) might be employed to study the complex process. Previously, we have shown that it is possible to remove the complicating equilibria of eq 1 by replacing the polybromide counterions of I-Br^+ with a non-nucleophilic triflate to yield I-Br^+/$SO_3CF_3^-$.[5] That species exhibits DNMR behavior dependent upon a remarkably fast degenerate exchange of Br^+ between I-Br^+ and added Ad=Ad (eq 2).[5] Herein we report the DNMR behavior

$$\text{I-Br}^+ + \text{Ad=Ad} \rightleftharpoons \text{Ad=Ad} + \text{I-Br}^+ \qquad (2)$$

for the more complex Ad=Ad/Br_2 system in DCE determined as a function of both temperature and [Br_2].

Results and Discussion

The ^1H NMR spectra of solutions with different concentrations of Ad=Ad and Br_2 in d_4-DCE were recorded at various temperatures using a Bruker 400-MHz spectrometer. In all the cases considered (see Table I) the Ad=Ad concentration was 10^{-3} M to 2×10^{-3} M with a large excess of Br_2 (0.17 to 1.25 M) thereby ensuring the quantitative formation of I-Br^+/Br^-_{2n-1}, with n = 2, 3, etc. For each sample, the spectra recorded at increasing temperatures exhibited a dynamic phenomenon involving the signals in the range between 2.1 and 2.6 ppm, the shapes of which changed between the extremes shown in Figure 1. The temperature at which these dynamic phenomena appeared increased markedly with increasing [Br_2].

The analysis and interpretation of the experimental data were developed through the following steps: (a) Spectral assignment for the limiting cases of slow and fast exchange (Figure 1, parts a and b). (b) Lineshape analysis for the

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[†] Present address: Dipartimento Scienze Chimiche, v.hA. Dorio 6, Catania 95125, Italy.

[‡] Present address: Department of Chemistry, Simon Fraser University, Burnaby, B.C.

(1) Strating, J.; Wieringa, J. H.; Wynberg, H. *J. Chem. Soc., Chem. Commun.* **1969**, 907.

(2) (a) Olah, G. A.; Hockswender, T. R., Jr. *J. Am. Chem. Soc.* **1974**, *96*, 3574. (b) Olah, G. A.; Schilling, P.; Westerman, P. W.; Lin, H. C. *Ibid.* **1974**, *96*, 3581.

(3) Ślebocka-Tilk, H.; Ball, R. G.; Brown, R. S. *J. Am. Chem. Soc.* **1985**, *107*, 4504.

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Table I. Experimental k_{NMR} Values Determined in d_4-DCE as a Function of Ad═Ad and Br_2 Concentrations and Temperature

$[Ad{=}Ad]_t \times 10^3$, M	$[Br_2]_t$, M	T, °C	k_{NMR},[a] s^{-1}
1.25	0.835	−6.2	2
1.25	0.440	−6.5	8
1.25	0.350	−6.5	12
1.25	0.285	−6.2	18
1.25	0.263	−6.5	20
1.25	0.225	−6.2	45
1.25	0.180	−6.2	65
1.25	0.170	−6.5	65
2.0	0.500	0.0	15
2.0	0.250	0.0	70
1.25	0.835	0.8	5
1.25	0.440	0.8	25
1.25	0.375	0.9	40
1.25	0.350	0.8	60
1.25	0.285	0.8	80
1.25	0.263	0.8	80
1.25	0.225	0.9	200
1.25	0.180	0.8	350
1.25	0.170	0.8	350
2.0	0.750	5.0	8
2.0	0.500	5.0	45
2.0	0.250	5.0	200
2.0	1.000	10	13
2.0	0.750	10	40
2.0	0.500	10	150
2.0	0.250	10	600
2.0	1.000	15	25
2.0	0.750	15	60
2.0	1.250	20	40
2.0	1.000	20	67
2.0	0.750	20	300
2.0	1.250	25	150
2.0	1.000	25	300

[a] Uncertainties estimated at ±10% of the k_{NMR} value up to 100 s^{-1} and ±20% of the value at ~300 s^{-1} (see text).

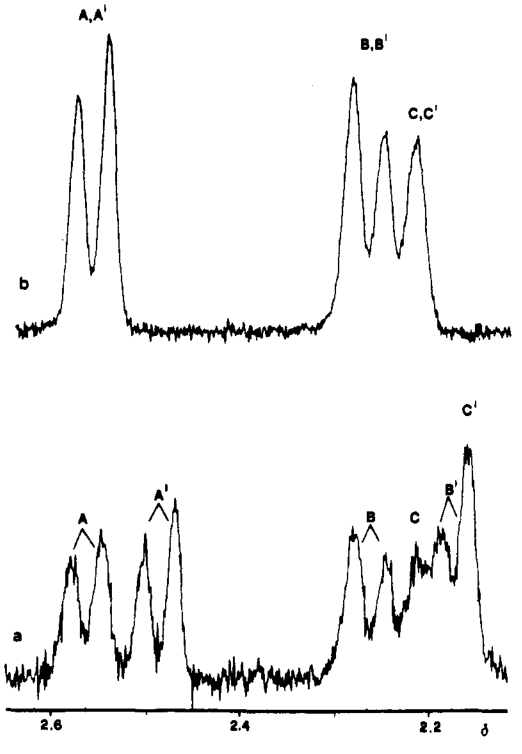

Figure 1. ^1H NMR spectra of d_4-DCE solutions of adamantylideneadamantane (2×10^{-3} M) and Br_2 (7.5×10^{-1} M) at (a) −10 °C and (b) +35 °C.

cases of intermediate exchange rates (Figure 3, parts d and e); this yielded a composite k_{NMR} constant, relating to the effective process observed for each spectrum analyzed. (c) Analysis of the empirical dependence of k_{NMR} on the temperature and on the analytical concentrations of Ad═Ad and Br_2 in each sample. (d) Formulation of an exchange mechanism able to explain the concentration and temperature dependence, allowing the analysis of the k_{NMR} values in terms of activation and equilibrium enthalpies and entropies. These five steps are detailed below.

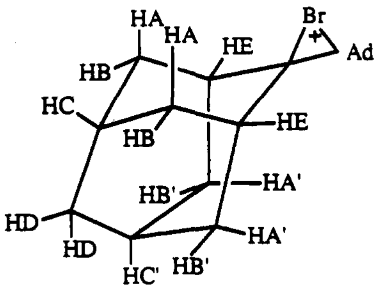

Figure 2. A diagram defining the locations of the various protons in $I\text{-}Br^+$. The designations A, A′, B, B′, etc. are not intended to identify spin systems but only to identify chemical shift equivalent protons at the slow exchange limit.

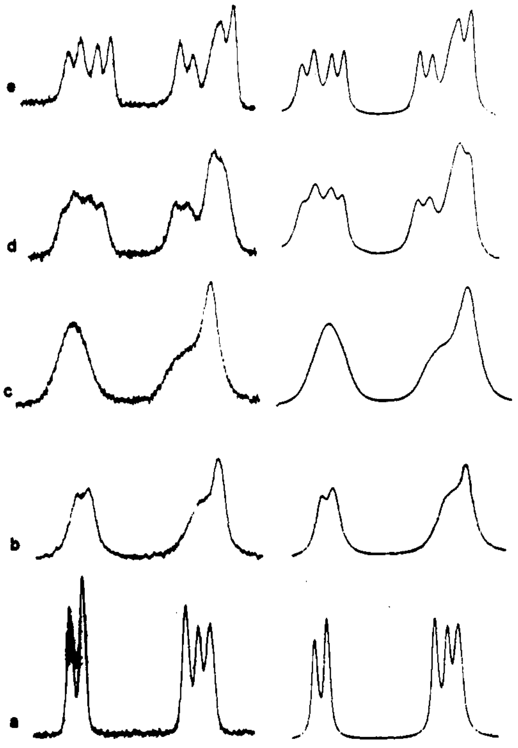

Figure 3. Experimental and calculated ^1H NMR spectra of $I\text{-}Br^+Br^-_{2n-1}$ in the 2.1–2.6 ppm spectral range: (a) $k_{NMR} = 5000$; (b) $k_{NMR} = 180$; (c) $k_{NMR} = 60$; (d) $k_{NMR} = 25$; (e) $k_{NMR} = 11$; all values in s^{-1}.

(a) Spectral Assignment. The pattern of the spectra recorded in the fast exchange limit (Figure 1b) is the same as was previously reported and analyzed[3,6] and corresponds to a system $I\text{-}Br^+/Br^-_{2n-1}$, where the various polybromide complexes are in rapid equilibrium.[7] Figure 2 shows the locations of the various protons, the chemical shifts of which are reported in Table II.

The spectrum reveals that the 28 ^1H nuclei in $I\text{-}Br^+/Br^-_{2n-1}$ are connected by three orthogonal symmetry

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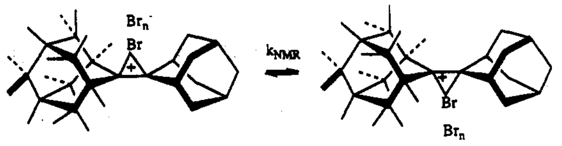
[6] There is a typographical error in Table of ref 3: H_D 2.04 should be under the right column.

Table II. ^{1}H NMR Chemical Shifts (ppm) for Ad=Ad (I) and I-$Br^+Br^-{}_{2n-1}$[a]

nucleus	I[b]	I-$Br^+Br^-{}_{2n-1}$ fast exchange limit	I-$Br^+Br^-{}_{2n-1}$ slow exchange limit
E	2.92	3.11	3.09
A,A′	1.90	2.53	2.568; 2.492
B,B′	1.66	2.23	2.260; 2.180
C,C′	1.83	2.20	2.233; 2.163
D	1.83	2.04	2.02

[a] All geminal coupling constants are $J = 12.5$ Hz. For assignment, see Figure 2. [b] Šlebocka-Tilk, H.; Ball, R. G.; Brown, R. S. *J. Am. Chem. Soc.* **1985**, *107*, 4504.

planes equivalent to those of Ad=Ad itself. The two perpendicular planes that contain, respectively, the three atoms of the bromonium ion, and only the Br^+, are true symmetry planes. However, a third perpendicular plane containing only the two carbons of the bromonium ring, can be an "effective" symmetry element arising from fast chemical exchange of the Br^+ between the two sides of the plane itself. The protons at opposite sides of this plane are syn and anti to bromine and are expected to have different chemical shifts. However, when the frequency of the transformation depicted in eq 3 is high relative to the maximum chemical shift difference between corresponding protons (e.g., H_A, H_A'; H_B, H_B'; etc.), they become equivalent.



(3)

When the temperature is lowered, the spectral pattern in the region between δ 2.1 and 2.6 ppm changes, until the slow exchange limit is reached, about 15 °C below the first observed broadening of the lines (Figure 1). The coupled doublets relating to protons A and B and the single line assigned to the protons C in the fast exchange limit are split into pairs of doublets and into a pair of lines, respectively, in the slow exchange limit; the lines from protons C are superimposed on the high-field doublet from protons B (see Figure 1 and Table II). This corresponds to the loss of the effective symmetry described in the case of fast exchange. In all cases the only coupling resolved is that between geminal nuclei. In order to complete the spectral assignment, we should specify which signals correspond to the nuclei closer to bromine, that is, which signals are to be attributed to syn and anti protons. This problem is unresolved, but fortunately the uncertainty does not influence the analysis and interpretation of the data.

An accurate inspection of various series of spectra recorded at temperatures below the slow exchange limit reveals that the relative chemical shifts of groups A, A′, B′, and C′ do not change throughout the range of temperatures and concentrations studied, but the chemical shifts of doublet B and singlet C show linear variations of 0.2 Hz/K and 0.04 Hz/K, respectively. No Br_2 concentration dependence of any chemical shift is found, showing that the various I-Br^+/$Br^-{}_{2n-1}$ species in rapid equilibrium do not differ significantly in chemical shift. The variable chemical shifts can be extrapolated to temperatures where the exchange is fast; the averaged chemical shifts computed on this basis are in excellent agreement with the experimental ones. This ensures the correctness of the extrapolation procedure used for determining the chemical shifts relative to the intermediate temperatures. The values of the coupling constants are independent of temperature and concentration.

(b) Lineshape Analysis. The lineshape analysis of the spectral region between δ 2.1 and 2.6 ppm was performed by means of the DNMR3 computer program[8] under the reasonable assumption that the exchange process monitored is most likely the one shown in eq 3.

Due to limitations of the DNMR3 program, the AA′, BB′, and the CC′ subspectra were computed separately, using the same kinetic constant k_{NMR}. The two subspectra were combined in a computer lineshape, which was fitted to the corresponding experimental spectrum by varying k_{NMR} in small steps. Examples of the excellence of agreement obtained are shown in Figure 3 for various typical rate constants.

Particular care was taken in the choice of the parameters determining the lineshapes in the limiting cases, because these may not be satisfactorily reproduced by only using one value for the effective relaxation time T_2^*. In fact, the experimental lines are non-lorentzian, being broadened by unresolved couplings which result in a half-height width of approximately 7 Hz. Such an effect is presumably negligible at the temperatures of major interest, where the broadening due to the chemical exchange is dominant. However, we checked this assumption by varying the values of the unresolved couplings between the nuclei involved in the exchange process until a good reproduction of the lineshape in the extreme cases was obtained. We could thus verify that the k_{NMR}'s obtained for the intermediate cases do not significantly differ from those found by using only one effective relaxation time ($T_2^* = 0.04$ s).

The rate constants finally determined are collected in Table I. The uncertainties are estimated to be roughly 10% of the constant up to values around 100 s^{-1} and about 20% of the k_{NMR} value when this is about 300 s^{-1}.

(c) Empirical Analysis of the k_{NMR} Rate Constants. From the data in Table I, it is clear that the exchange process becomes dramatically slower as the [Br_2] increases. The exchange rate was also found to be independent of [Ad=Ad] by examining the ^{1}H NMR spectra of solutions containing 1.0 M [Br_2] and 5×10^{-4} to 2×10^{-3} M [Ad=Ad]. For all these solutions, the spectra recorded at the same temperatures were identical. Finally, the appearance of the spectra indicates that the temperature interval between the fast and slow exchange limits is unusually narrow (~15 °C). The fitting of the experimental k_{NMR} values was tried with a function which empirically combines the temperature dependence suggested for the kinetic constants by the Eyring equation with the observed dependence on the Br_2 concentration. In effect, eq 4:

$$k_{NMR} = ATe^{-(X/RT)}[Br_2]^y \qquad (4)$$

with A, X, y as adjustable parameters, allowed a good reproduction of the k_{NMR} values. The three fitting

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(7) For $n = 1$, a charge-transfer complex (CTC) instead of a 1:1 ionic complex is expected,[4] and its NMR spectrum (not detected) should closely resemble that of Ad=Ad (described in ref 3). In the present work, no spectral evidence for any 1:1 complex was ever observed because the [Br_2] was kept in large excess of the [Ad=Ad] forcing higher order polybromide species to be dominant.

(8) Kleier, D. A.; Biusch, G. *Quantum Chem. Progr. Exch.* **1970**, *10*, 165.

parameters could be simultaneously determined only by using the logarithmic form (eq 5) of eq 4, since in this way

$$\ln k_{\mathrm{NMR}} = \ln AT - X/RT + y \ln [\mathrm{Br_2}] \qquad (5)$$

the dramatically high correlation between A and X is in part removed. We found ln A = 47(2), X = 28.2(1.1) kcal/mol, and y = −2.6(0.1), the rms error computed for the k_{NMR} values being 32 s^{-1}. The value of y immediately suggests that any exchange mechanism compatible with the experimental evidence must contain both a $[\mathrm{Br_2}]^{-2}$ and a $[\mathrm{Br_2}]^{-3}$ dependence. It must be noted that neither setting $y = -2$ nor $y = -3$ in eq 4 (or 5) led to a satisfactory fit of the experimental k_{NMR} values.

(d) The Exchange Mechanism. The kinetic constant k_{NMR} expresses the frequency of the process shown in eq 3 for each molecule, or complex unit, undergoing the transformation. The k_{NMR} is therefore simply connected to the rate of this transformation, ν, expressed in molar concentration per second:

$$\nu = k_{\mathrm{NMR}}[\mathrm{complex}] \qquad (6)$$

The complex concentration consists of the total concentration of all the **I-Br$^+$Br$^-_{2n-1}$** species in fast equilibrium in the solution:

$$[\mathrm{complex}] = [\mathrm{C_1}] + [\mathrm{C_2}] + \ldots [\mathrm{C}_n] \qquad (7)$$

In order to justify the empirical dependence of k_{NMR} on the temperature and Br$_2$ concentration, it must be assumed that the rate-determining step of the dominant exchange mechanism is the interconversion of a 1:1 complex, Ad═Ad/Br$_2$. At this stage, the data do not allow an unambiguous interpretation of the structure of the 1:1 complex, although a most reasonable candidate is the CTC[4] (*vide infra*). Nevertheless, this assumption allows the following statements:

$$\nu \cong \mathrm{d}[\mathrm{Ad{=}Ad/Br_2}]/\mathrm{d}t = k_0[\mathrm{Ad{=}Ad/Br_2}] \qquad (8)$$

where k_0 can be expressed by the Eyring equation

$$k_0 = f_0 \frac{k_{\mathrm{B}}}{h} \mathrm{T} \mathrm{e}^{-(\Delta H^{\ddagger}_0 - T\Delta S^{\ddagger}_0)/RT} \qquad (9)$$

and the statistical factor f_0 measures the probability that the reaction transforms anti to syn protons.

After substitution of eq 7 into eq 6 and combination of the resulting expression with eq 8, we obtain

$$k_{\mathrm{NMR}} = \frac{k_0[\mathrm{Ad{=}Ad/Br_2}]}{[\mathrm{C_1}] + [\mathrm{C_2}] + [\mathrm{C_3}] + [\mathrm{C_4}] + \ldots} \qquad (10)$$

Each concentration $[\mathrm{C}_n]$ can be expressed as a function of [Ad═Ad] and [Br$_2$] through the equilibrium constant K_n for the complex formation (eq 11, where n = 1, 2, 3, 4, etc.):

$$[\mathrm{C}_n] = K_n[\mathrm{Ad{=}Ad}][\mathrm{Br_2}]^n \qquad (11)$$

By substitution into eq 10 and obvious rearrangement we have:

$$k_{\mathrm{NMR}} = \frac{k_0 K_1/K_3}{\mathrm{K_1/K_3 + K_2/K_3[Br_2] + [Br_2]^2 + K_4/K_3[Br_2]^3}} \qquad (12)$$

where terms up to n = 4 have been retained. In fact, in order to explain the empirical dependence of k_{NMR} on $[\mathrm{Br_2}]^{-2.6}$, it is necessary to assume that an appreciable quantity of **I-Br$^+$** is present in solution as a Br$_7^-$ salt. The existence of polybromide ions of this type, and also of higher species, is known,[9] and these are favored under conditions of high [Br$_2$]. On the basis of the known values of the stability constants K_1, K_2, and K_3,[4] the first term K_1/K_3, in the denominator of eq 12 can be safely ignored. Furthermore, the second term, $K_2/K_3[\mathrm{Br_2}]$, can be neglected in the investigated Br$_2$ concentration range, so that eq 12 can be simplified to eq 13. The analytical form

$$k_{\mathrm{NMR}} = \frac{k_0 K_1/K_3}{[\mathrm{Br_2}]^2 + K_4/K_3[\mathrm{Br_2}]^3} \qquad (13)$$

of eq 13 is such that, with suitable parameters, it will reproduce the experimental k_{NMR} values as well as eq 4 does. On the other hand, choosing the formation enthalpies and entropies of the various complexes as fitting parameters should allow a check of the consistency of the proposed mechanism with what was already known about the system under investigation (see later). The relevant parameters are contained in k_0, through eq 9, and in K_1, K_3, K_4, through eq 14:

$$K_n = \mathrm{e}^{-(\Delta H_n - T\Delta S_n)/RT} \mathrm{A}_n \qquad (14)$$

A_n differs from 1.0 only if the activity coefficients for the various species in equilibrium are not unity. ΔH_n and ΔS_n (which are considered independent of temperature) are the enthalpy and entropy of formation of the complexes of Ad═Ad with nBr$_2$ molecules (the reference states for the reactants and products is a 1 M solution).[10] Equation 13, therefore, can be rewritten as:

$$k_{\mathrm{NMR}} = \frac{\frac{k_{\mathrm{B}}}{h} T X_1 \mathrm{e}^{-(X_2/RT)}}{[\mathrm{Br_2}]^2 + X_3 \mathrm{e}^{-(X_4/RT)}[\mathrm{Br_2}]^3} \qquad (15)$$

where

$$X_1 = f_0(A_1/A_3)\mathrm{e}^{(\Delta S^{\ddagger}_0 + \Delta S_1 - \Delta S_3)/R} \qquad (16)$$

$$X_2 = \Delta H^{\ddagger}{}_0 + \Delta H_1 - \Delta H_3$$

$$X_3 = (A_4/A_3)\mathrm{e}^{(\Delta S_4 - \Delta S_3)/R}$$

$$X_4 = \Delta H_4 - \Delta H_3$$

In principle, X_1, X_2, X_3 and X_4 can be determined by fitting the experimental k_{NMR} values to those computed by means of eq 15. In practice, the high correlation between X_3 and X_4 forces an assignment of a fixed value to one of these variables. Neither can reasonably be taken to be 0, since the formation of higher aggregates must be accompanied by a loss of entropy and a gain of enthalpy. Data available for the tetrabutylammonium–polybromide system[9b] suggest a range of −5 to −10 eu for $\Delta S_4 - \Delta S_3$.

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[9] (a) *Gmelin Handbook of Inorganic Chemistry, Bromine*, Springer-Verlag: Berlin, 1985; Suppl. Vol. A, p 520. (b) Bellucci, G.; Bianchini, R.; Chiappe, C.; Ambrosetti, R. *J. Am. Chem. Soc.* **1989**, *111*, 199.

[10] In principle, all these thermodynamic parameters could be determined independently from UV-vis spectrophotometric measurements. In practice, however, this is impossible because of the very high Br$_2$ concentrations required to generate the Br$_7^-$ species and of the overlap of its absorption with those of the other species present.

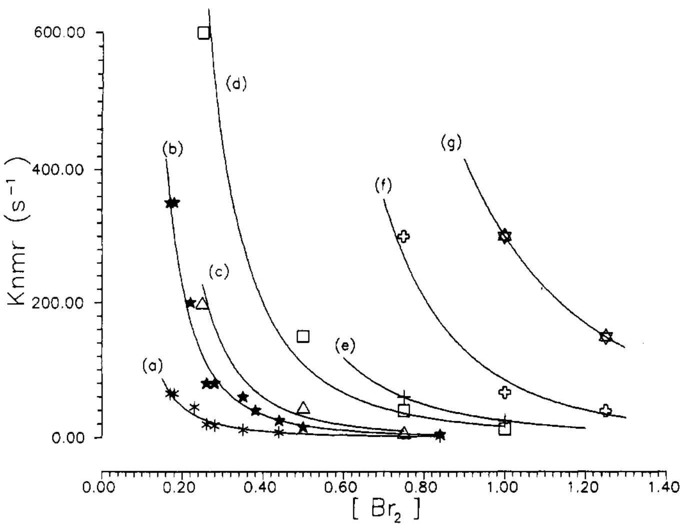

Figure 4. Experimental values of k_{NMR} versus [Br$_2$]. Continuous curves are drawn according to eq 15 for data at (a) −6.5 to −6.2; (b) 0–0.9; (c) 5; (d) 10; (e) 15; (f) 20; and (g) 25 °C.

Table III. Computed Values of X_1, X_2, and X_4 Derived from the Fitting of the k_{NMR} Data of Table I to Eq 15 Assuming Two Fixed Values for X_3

	$X_3 = 8.07 \times 10^{-2}$ ($\Delta S_4 - \Delta S_3 \simeq -5$ eu)		$X_3 = 6.52 \times 10^{-3}$ ($\Delta S_4 - \Delta S_3 \simeq -10$ eu)	
X_1	$1.5 \times 10^{13} (3.6 \times 10^{14})$		$0.7 \times 10^{13} (1.5 \times 10^{14})$	
X_2	26.2(1.3) kcal/mol		25.7(1.2) kcal/mol	
X_4	−1.65(0.30) kcal/mol		−3.12(0.29) kcal/mol	
$\Delta H_0^\ddagger + \Delta H_1$	ΔH_3	ΔH_4	ΔH_3	ΔH_4
0	−26.2	−27.8	−25.7	−28.8
5	−21.2	−22.8	−20.7	−23.8

With $A_4/A_3 = 1$,[11] these limits correspond to $X_3 = 8.07 \times 10^{-2}$ and $X_3 = 6.52 \times 10^{-3}$, respectively. Using these two values for X_3, the fitting procedure terminated with an RMS error of 33 and 32 s^{-1}, with most of the error resulting from the highest k_{NMR} values. Shown in Figure 4 is a representation of all of the experimental data fit to the lines generated on the basis of eq 15. The best fit values for X_1, X_2, and X_4, using the two fixed values above for X_3, are summarized in Table III.

X_2 and X_4 are analyzable in terms of the enthalpic profile for the proposed exchange mechanism that is sketched in Figure 5, where $\Delta H_0^\ddagger$ represents the activation enthalpy for the kinetic process, and ΔH_1, ΔH_3 refer to the association enthalpies for the 1:1 and 1:3 Ad=Ad·Br$_2$ complexes relative to free Ad=Ad and Br$_2$. $\Delta H_0^\ddagger + \Delta H_1$ is the activation energy for the formation of the 1:1 complex from Ad=Ad and Br$_2$ and cannot be negative. Its valve cannot be large either, since the complex formation is too fast to be observed with fast kinetic techniques. A value between 0 and 5 kcal/mol seems therefore to be reasonable. On this basis ΔH_3 should range between −26 and −21 kcal/mol. The former value is in reasonable agreement with a preliminary spectrophotometric evaluation, giving $\Delta H_3 = -29 \pm 3$ kcal/mol. Moreover, since $X_4 = \Delta H_4 - \Delta H_3$, a value of −23 to −29 kcal/mol can be calculated for ΔH_4.

X_1 mainly depends upon a combination of entropic factors. Assuming $f_0 A_1/A_3 \simeq 0.5$–1.0 (see ref 11) it follows that $\Delta S_0^\ddagger + \Delta S_1 - \Delta S_2 \simeq -59$ to -62 eu, a reasonable value for a process involving multiple associations.

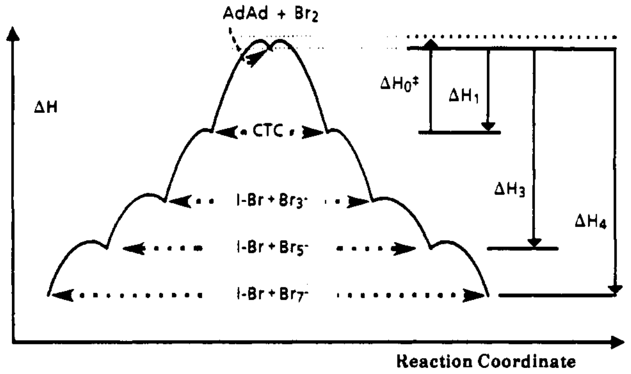

Figure 5. Energy profile for the interconversion of the complexes of Ad=Ad with Br$_2$.

The above analysis, while being only approximate, is internally consistent with the proposed mechanism for bromine site exchange and with what is known about the Ad=Ad/Br$_2$ system[3,4] and the behavior of polybromide ions in solution.[9] Qualitatively, that the exchange rate decreases so markedly with increasing [Br$_2$] is easily visualized from the enthalpic profile given in Figure 5. Such increases in [Br$_2$] convert more of the total complex in solution into the lower energy Br$_5^-$ and Br$_7^-$ components, thereby decreasing the amount of 1:1 complex from which the exchange phenomenon occurs. As stated previously, the available evidence consistent with the dependence of the k_{NMR} values on [Br$_2$] suggests that it is the 1:1 complex that is responsible for the exchange process. Of the two possible candidates for the essential 1:1 complex, for the following reasons we prefer the CTC although the kinetics do not rule out a bromonium ion/Br$^-$ species. First, abundant evidence for the formation of the Ad=Ad/Br$_2$ CTC in DCE exists,[4] as does evidence for the CTC's of other olefins under a variety of conditions.[12] However, no evidence for the formation of detectable quantities of a bromonium ion/Br$^-$ pair in DCE exists. Furthermore, available evidence for the $Br^- + Br_2 \rightleftharpoons Br_3^-$ equilibrium suggests that the formation constant is immeasurably large, being $\geq 2 \times 10^7$ M^{-1}.[13] Thus, at 25 °C, and assuming an insensitivity to the nature of the cationic counterion,[4] the free energy of the bromonium ion/Br$^-$ species would be at least 10 kcal/mol above the tribromide, 6 kcal/mol above the CTC, and 2.5 kcal/mol above the free olefin + Br$_2$.[14] These computed values seem large enough that the bromonium ion/Br$^-$ pair is a high energy intermediate and that any transition states leading through it also be of higher energy than the free olefin + Br$_2$. While this does not absolutely exclude its involvement in the exchange process, it would require that rate-limiting step for the exchange process is the interconversion of I-Br$^+$/Br$^-$ and the CTC as in eq 17, with all other steps being

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(11) This assumption is not crucial, because A_4/A_3 cannot be very different from unity, and the range of variability of X_3 resulting from the assumed $\Delta S_4 - \Delta S_3$ extreme values is more than 1 order of magnitude.

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(14) This calculation derives from equilibrium constants at 25 °C for $Ad{=}Ad + Br_2 \rightleftharpoons$ CTC ($K_1 = 289$ M^{-1}),[4] $Ad{=}Ad + Br_2 \rightleftharpoons$ bromonium ion/Br$_3^-$ ($K_{12} = 3.23 \times 10^5$ M^{-2})[4] and CTC + Br$_2 \rightleftharpoons$ bromonium ion/Br$_3^-$ ($K_{12}/K_1 = 1.12 \times 10^3$ M^{-1}).[4]

$$\mathrm{Ad{=}Ad} + \mathrm{Br_2} \overset{\text{fast}}{\rightleftharpoons} \mathrm{CTC} \overset{\text{slow}}{\rightleftharpoons} \mathrm{I\text{-}Br^+/Br^-} \underset{-\mathrm{Br_2}}{\overset{+\mathrm{Br_2(fast)}}{\rightleftharpoons}} \mathrm{I\text{-}Br^+/Br_3^-} \quad (17)$$

fast. This seems unlikely, since under this hypothesis, the rate-limiting step for the formation of the ionic forms would be the uncatalyzed ionization of the CTC followed by rapid bimolecular interception of I-Br^+/Br^- by free Br_2. Since it is well known that electrophilic bromination of any presently investigated olefin in DCE is bimolecular in $[Br_2]$,[12g,15] spontaneous ionization of the CTC to a bromonium ion/Br^- ion pair in those cases cannot be rate limiting. In the absence of additional evidence, it seems unwarranted to suggest such a process for the Ad=Ad/Br_2 system.

In conclusion, it is reasonable to accept that the Ad=Ad/Br_2 system can be taken as a representative example of a broad class of olefins that have been shown[12e,15,16] to undergo extensive reversal to reagents during their electrophilic bromination. Although Ad=Ad cannot proceed past the stage of bromonium ion formation, the stages of the reaction up to that must be considered as normal. If so, we can state that in agreement with microscopic reversibility the rate determining step for that reversal involves, in general, an intermediate having 1:1 (olefin/Br_2) stoichiometry, and that this species is very likely the charge-transfer complex.

Experimental Section

Although adamantylideneadamantane (I) can be made and purified as previously described,[3] we have found it is more convenient to use the McMurry coupling[17] of adamantanone. The crude product (~70% yield) can be recrystallized from MeOH to yield ~50% of colorless crystals (mp 185–186 °C; lit.[15] 184–186 °C). 1,2-Dichloroethane-d_4 (Cambridge Isotope Laboratories, 99% D) was distilled (for azeotropic removal of any H_2O present) prior to use. Bromine (Fluka AG) was used as supplied.

All NMR solutions were prepared immediately before use and kept in the dark during manipulations. The [Ad=Ad] varied from 10^{-3} M to 2×10^{-3} M and the $[Br_2]$ was in large excess (0.17–1.25 M). ^1H NMR spectra were recorded using a Bruker 400-MHz machine. The temperature inside the probe was measured as precisely as possible by inserting a thermocouple into an NMR tube containing toluene-d_8 which was then lowered into the probe. This was left in the probe for 10–15 min to equilibrate prior to obtaining a reading. At the completion of the NMR spectrum, the probe temperature was again measured in the same way to ensure that minimal drift had occurred. Typically, a drift of 0.3 °C was considered acceptable, and the temperature was considered to be the average of the initial and final readings.

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