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Concentration Dependence of the Steric Course of Bromine Addition to Acenaphthylene. A Product and Kinetic Study‡

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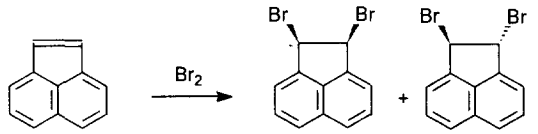
Abstract: The ratios of Z- to E-1,2-dibromo-1,2-dihydroacenaphthylene obtained in the bromination of acenaphthylene in chlorinated solvents have been determined by NMR as a function of the reagents concentrations. Kinetic measurements have shown that always the reaction occured through the same rate-determining step. A rationalization involving tight or solvent-separated ion pairs intermediates, is proposed. Copyright © 1996 Elsevier Science Ltd

In spite of the extensive studies devoted to the mechanism of electrophilic bromination of olefins,[1] new investigations[2] are bringing to light new important features which modify the traditional picture of this reaction. Many mechanistic results on the electrophilic addition to the double bond are related to the first steps of the reaction, in which the ionic intermediate is formed, even if several factors appear to be implicated in the product-determined step, and a few of which are not completely clear. The exclusive anti addition found in the bromination of unconjugated olefins is considered to be related to the fully bridged nature of the intermediate,[3] while the formation of both anti and syn dibromo adducts in the Br_2 addition to aryl olefins is generally attributed to the involvement of open intermediates.[2] The stereochemistry of the bromine attack on the carbocations should depend on their lifetimes and arises from a competition between conformational equilibration and nucleophilic trapping of the intermediates.[2] On the other hand, the possibility of a direct syn collapse of the bromocarbonium-bromide (or polibromide) ion pair intermediate has been also suggested.[4] Furthermore, recent data on the selectivity of product formation in the bromination of *cis*- and *trans*-stilbene have shown[5,6] that the stereoselectivity of the corresponding dibromide is solvent- and concentration-dependent.

Considering that preliminary results reported[7] by Russian workers showed that acenaphthylene adds molecular halogen nonstereospecifically we have undertaken a systematic investigation of the effects of the reagent concentrations on the steric course of the bromination of acenaphthylene (**1**) in aprotic chlorinated solvents.



1 **2** **3**

‡Dedicated to the memory of Professor Giuseppe Bellucci (d. March 3, 1996).

On the basis of the product distribution data and kinetics measurements we propose a rationalization involving tight or solvent-separated ion pairs intermediates determining the syn and anti addition in the product determining step of this reaction.

Results

Product Distributions. The ratios of *Z*- to *E*-1,2-dibromo-1,2-dihydroacenaphthylenes (**2** and **3**) determined by ^{1}H NMR for the bromination of acenaphthylene (**1**) in dichloromethane-d_2 (DCM) and chloroform-*d* at 0 °C are reported in Table 1. The reaction were carried out by fast mixing precooled equal volumes of the solutions of the two reagents at the required concentrations and the products were analyzed immediately after.

Table 1. Distribution of *Z*- (**2**) to *E*-1,2-dibromo-1,2-dihydroacenaphthylene (**3**) in Bromination of Acenaphthylene (**1**) in Dichloromethane-d_2 (DCM) and Chloroform-*d* at 0 °C.

Run	[Br_2]	[**1**]	Solvent	% Dibromide	
	M	M		**2**	**3**
1	0.4	0.4	DCM	33	67
2	0.04	0.04	DCM	30	70
3	0.4	2	DCM	68	32
4	0.4	1	DCM	70	30
5	0.04	0.2	DCM	30	70
6	1	0.4	DCM	13	87
7	0.2	0.2	$CHCl_3$	47	53
8	0.02	0.02	$CHCl_3$	50	50
9	0.2	0.02	$CHCl_3$	50	50
10	0.2	1	$CHCl_3$	56	44

Both stoichiometric reactions and runs in which one component was in large excess were examined. The **2** to **3** product ratios did not change significantly with proceeding of the reaction showing that the products were stable under the reaction conditions.

The reactions of **1** in chloroform were practically lacking in steoreoselectivity at all the reagent concentrations (runs 7-10), while a 30:70 stereoselection in favour of the E-isomer was observed when the 1:1 reactions were carried out in the more polar DCM, independent of the reagent concentrations (runs 1,2). Identical stereochemical results were obtained when the brominations in DCM were carried out with an excess of one reagent being the other one at sufficiently low concentration (run 5). An increase in the stereoselection in favour of the E-isomer was instead observed in this solvent at high olefin concentration, 0.4 M, in the presence of an excess of Br_2 (run 6). On the other hands, the runs in which an an excess of **1** occurred, at [Br_2]≥ 0.2 M, exhibited an inversion in the **2**:**3** ratio (runs 3, 4).

Kinetic Measurements. The kinetic constants for the bromine addition to acenaphthylene (**1**) were first determined in 1,2-dichloroethane (DCE) using a stopped-flow apparatus, both at identical reagent concentration (*ca.* 5 x 10^{-3} M) and with a large excess of olefin, monitoring the disappearance of the visible

absorption band of the halogen. A third-order and pseudo-second-order rate laws (eq 1) were respectively obeyed up to over 90% conversion, as usually found for olefin bromination in aprotic, chlorinated solvents.[8]

$$-d[Br_2]/dt = k_3 [Br_2]^2[Ol] \qquad (1)$$

In order to determine the activation parameters of this reaction, the kinetics were followed at six temperatures between 8 and 60 °C. The average third-order rate constants are reported in Table 2, which also includes the apparent activation parameters.

Table 2. Rate Constants for the Bromination of **1** in DCE in the 8-60 °C Temperature Range and the Apparent Activation Parameters.

T °C	k_3 (M^{-2} s^{-1})	$E_{a(obsd)}$ (kcal mol^{-1})	$\Delta H^{\neq}$ (kcal mol^{-1})	$\Delta S^{\neq}$ (eu)
8	3.55 (0.15) 10^5			
15	2.50 (0.10) 10^5			
25	2.20 (0.10) 10^5	-3.73 (0.2)	-4.30 (0.2)	-49 (1)
38	1.50 (0.10) 10^5			
50	1.35 (0.05) 10^5			
60	1.20 (0.05) 10^5			

The apparent negative activation energy, $E_{a(obsd)}$ = -3.73 kcal mol^{-1}, is consistent with the involvement of exothermic preequilibrium steps followed by the rate determining ionization,[8a] while the large and negative entropy factor, $\Delta S^{\neq}$ = -49 e.u. agrees with a termolecular transition state.

The influence of the solvent polarity on the rates of bromination of **1** has been investigated carrying out the reactions in mixtures of DCE and chloroform. In all solvent mixtures the free Br_2 reactions obeyed eq 1 and the related rate constants are reported in Table 3.

Table 3. Rate Constants for the Bromination of **1** in Mixtures of DCE and Chloroform at 25 °C.

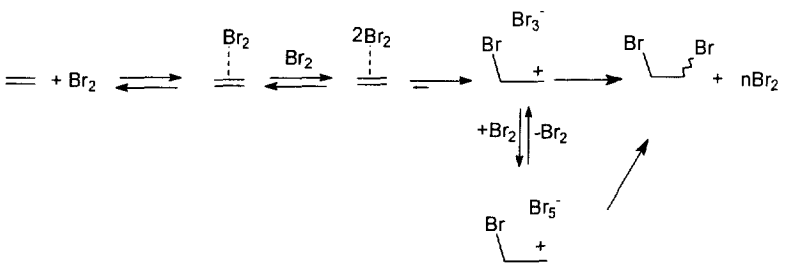
% DCE	ε	k_3 (M^{-2} s^{-1})
100	10.697	2.20 (0.10) 10^5
80	9.188	1.17 (0.10) 10^5
50	7.184	5.90 (0.10) 10^4
20	5.629	2.60 (0.10) 10^4
0	4.616	9.50 (0.10) 10^3

A very satisfactory linear plot (r = 0.998), with a large and positive slope (35.5) indicating a markedly ionized dipolar transition state, was obtained on plotting $\ln k_3$ (of Table 3) versus the Kirkwood function $(\varepsilon-1)/(2\varepsilon+1)$.[9]

Discussion

The constancy of the **2** : **3** ratios during each single run of the **1** bromination and the stability of the *E*- and *Z*-dibromides under the reaction conditions exclude the possibility that the concentration dependence of the steric course of the Br_2 addition to **1** was due to dibromide isomerization. Furthermore, the kinetic measurements (Table 2 and 3) also rule out the possibility that the two dibromides can arise from reactions of different kinetic order. Indeed, the bromination of **1** follows a clean third-order rate law, both in DCE and chloroform, consistent with the generally accepted mechanism for the Br_2 addition in aprotic solvents, involving the slow ionization of 1:2 olefin Br_2 π complex, formed in a preequilibrium step, to give a bromonium (bromocarbonium)-tribromide ion pair intermediate, which then collapses to dibromide and molecular bromine.

Scheme 1



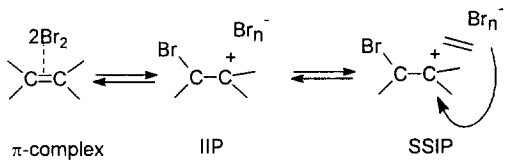
Whether the intermediate ions are symmetrically or asymmetrically bridged, or open β-bromocarbonium ions, depends upon the ability of the cationic moiety to stabilize a positive charge on the carbon, stabilization that in the case of olefin **1** is given by the conjugation of the benzylic carbocation centre with the naphtalene system. The β-bromocarbonium formulated in Scheme 1 is in reality a degenerate pair of cations with a bridged structure as intermediate. Furthermore, since it has been shown[10] that with 1,2-diaryl substituted olefins the reversibility of the ionization of the olefin-Br_2 π complexes to ion pairs depends on the bridged or open nature of the cationic moiety, bridged bromonium ions being more prone to return, in the bromination of **1** the electrophilic step should be practically completely rate determining. Therefore the decrease in k_3 for the Br_2 addition with decreasing polarity reported in Table 2 and 3 mainly reflects an increasing difficulty in the ionization step of the mechanism shown in Scheme 1. Furthermore, the excellent linear dependence of the $\ln k_3$ on the Kirkwood function of the dielectric constant in mixtures of DCE and chloroform conclusively shows that the same polar mechanism operates also in a such poorly polar solvent as the latter. Since the stereoselectivity of the reaction towards the formation of *Z*-dibromide, under the same conditions, increases with decrease in the polarity of the solvent this behaviuor cannot be due to change involving the rate determing step, i.e. the ionization step.

The solvent and concentration dependence of the steric course of the Br_2 addition to **1** can then only arise from a change in nature or mode of collapse of the ionic intermediate. In principle, the anionic moiety could be involved in this change when the Br_2 concentration is varied. A set of equilibria preeceding the last-product forming step of Scheme 1 have been analyzed by UV-vis and ^1H NMR spectroscopy[11] using the adamantylideneadamantane system. These investigations have, in particular, shown the existence of an equilibrium between tribromide and pentabromide in the anionic moiety of the ion pairs, at sufficiently high

Br_2 concentrations. On the other hand, the reagent concentrations also affects the ion pairs association and dissociation and the translocation of the counteranion.

In the low polar chloroform the ionic intermediates are surely formed in the rate-determining step as tight ion pairs and the translocation of the counteranion in these conditions can be sufficiently slow, since an increase in the distance of the two electrostatically bound ion should occur during this process, that a large amount of syn collapse to give the dibromide **2** occurs at all the examined reagent concentrations (runs 7-10). On the other hand, increasing the solvent polarity a progressive change from intimate to solvent-separated ion pairs may occur, at least at the lower reagent concentrations, which could allow for a longer lifetime of the intermediate, and therefore for a more extensive translocation of the counteranion before collapse, leading to an increase of *E*-dibromide **3** in the reactions carried out in DCM (runs 2,5). Intimate and solvent ion pairs have been shown in solvolytic studies of secondary halides and sulfonates even in non protic solvents like acetonitrile. The intimate or tight ion pairs (IIP) give products with retention of configuration while the solvent separate ion pair (SSIP) give products with inversion of configuration likely by a SN2 like transition state.[12]

Scheme 2



In the same solvent, however, an increase in reagent concentrations, disfavouring ion pairs dissociation, again favour the syn collapse and raises the *Z*-dibromide **2** at least when the reactions are carried out in the presence of higher olefin concentrations (runs 3,4). Indeed high Br_2 concentrations not only favour the tight ion pairs but also displace the equilibrium of the counteranion towards more charge-diffused and less reactive polibromide species (Br_5^- or Br_7^-) which, having probably a L-shape,[13] are able to locate a Br^- ready for the anti attack without translocation of the counteranion. This behaviour could then counterbalance the ion pairs association effect increasing again the E-dibromide formation (runs 1,6).

Experimental

^1H NMR spectra were registered in $CDCl_3$ and CD_2Cl_2 with a Bruker AM 360 instrument containing TMS as the internal reference. Kinetic measurements performed with a previously described[14] stopped-flow apparatus equipped with a parallel diode-array detector.

Bromine (1 ml sealed ampules, C. Erba > 99.5%) and 1,2-dichloroethane (Fluka > 99.5 %) were used as supplied. Acenaphthylene (Aldrich) was converted to its picrate and recrystallized from ethanol. It was then freed of picrate acid by distribution between dichloromethane and aqueous sodium bicarbonate and finally recrystallized from ethanol.

Bromination Procedure

Solvent and Concentration Dependence of Product Distribution. Precooled (0 °C) CD_2Cl_2 or $CHCl_3$ solutions of Br_2 (0.5 ml) of concentration ranging between 2 and 0.04 were rapidly mixed with equal volumes of 4-0.04 M precooled solutions of olefins **1** in the same solvent, and the reaction mixtures were maintained

in the dark and analyzed by NMR. The reagents concentrations after mixing are reported in Table 1. The **2**:**3** ratios was determined on the basis of the benzyl signals in the ^1H NMR spectra. All the reactions were carried out in triplicate. The ratios reported in Tables I were reproducible within ± 2%. All the product ratios were independent of the percent of conversion. The stability of dibromides **2** and **3** in the presence of the halogen was checked by exposing dibromide mixtures to Br_2 under conditions identical with those employed in the bromination reactions, following by NMR analysis.

Kinetic Measurements. 1,2-Dichloroethane, chloroform and 1,2-dichloroethane-chloroform Br_2 solutions (1.2×10^{-2} M), prepared shortly before use, were protected from the daylight and adjusted to twice the desidered initial concentrations in the kinetic runs. Aliquotes of these solutions, prethermostated at the temperatures reported in Table 2, were mixed with equal volumes of prethermostated solutions of olefins **1** of suitable concentrations (1.2×10^{-2} - 1.5×10^{-1} M). Temperature control was ensured by the mixing device of apparatus, consisting of a Sf-3L Hi-Tech support unit. In all solvents, kinetic constant were calculated at several wavelengths on the basis of the disappearance of the free bromine absorption band in the 350-450 nm interval. The absorbance/time data were fitted to the appropriate third-order or pseudo-second-order equations. All reactions were carried our at least in triplicate. The kinetic constants are reported in Table I. The apparent activation parameters, reported in Table 2, were obtained from Arrhenius plots.

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REFERENCES

1. a) Schmid, G. H.; Garrat, D. G. *The Chemistry of Double-Bonded Functional Groups*; Patai, S., Ed.; Wiley; New York, 1977; Suppl. A, Part 2, p 725. b) De la Mare, P. B. D.; Bolton, R. *Electrophilic Additions to Unsaturated Systems,* 2nd ed.; Elsiever: New York, 1982; p 136. c) V'yunov, K. A.; Guniak, A. I. *Russ. Chem. Rev.(Engl. Trans.)* **1981**, *50*, 151.
2. For recent reviews see: a) Schmid, G.H., *The Chemistry of Double-Bonded Functional Groups,* ed. S. Patai, Wiley, New York, 1989; Suppl. A, Vol.2 part 1, p.699. b) Ruasse, M.F. *Adv. Phys. Org. Chem.* **1993**, *28*, 207.
3. Roberts, I; Kimball, J. E. *J. Am. Chem. Soc.*, **1937**, *59*, 947.
4. Barili, P. L.; Bellucci, G.; Marioni, F.; Morelli, I.; Scartoni, V. *J. Org. Chem.* **1973**, *38*, 3472. Heasly, G. E.; Bower, T. R.; Dougharty, K. W.; Easdon, J. C. *J. Org. Chem.* **1980**, *45*, 5150.
5. Bellucci, G.; Bianchini, R.; Chiappe, C. ; Marioni, F. *J. Org Chem.* **1990**, *55*, 4094.
6. Bianchini, R.; Chiappe, C. *J. Org Chem.* **1992**, *57*, 6474.
7. Anikin, V. F.; Levandovskaya, T. I. *J. Org. Chem. USSR.* **1988**, *5*, 961.
8. a) Bellucci, G.; Bianchini, R.; Ambrosetti, R. *J. Am. Chem. Soc.* **1985**, *107*, 2464. b) Bellucci, G.; Chiappe, C.; Marioni, F. *J. Am. Chem. Soc.* **1987**, *109*, 515.
9. Kirkwood, J. G. *J. Chem. Phys.* **1934**, *2*, 351.
10. Bellucci, G.; Bianchini, R.; Chiappe, C.; Brown, R.S.; Slebocka-Tilk, H. *J. Am. Chem. Soc.* **1991**,*113*, 8012.
11. Bellucci G.; Bianchini, R; Chiappe, C.; Marioni, F.; Ambrosetti, R.; Brown, R.S.; Slebocka-Tilk, H. *J. Am. Chem. Soc.* **1989**, *111*, 2640. Bellucci G.; Bianchini, R; Chiappe, C.; Ambrosetti, R.; Catalano, D; Bennet, A.J.; Slebocka-Tilk, H.; Aarts, G. H. M.; Brown, R.S. *J. Org. Chem.* **1993**, *58*, 3401.
12. bentley, T. W. and Schleyer, P. v. R. *Progress in Phys. Org. Chem.*, **1977**, *14*, 1.
13. a) An L-shape was found for the pentaiodide anion. Broekema, J.; Havinga, E. E.; Wieberg, E. H: *Acta Crystallogr.* **1957**, *10*, 596. b) A recent ab-initio calculation shows an L-shaped structure for the ethylene-Br_2 Br_2 complex. To be published.
14. Ambrosetti, R.; Bellucci, G.; Bianchini, R.; Fontana, E.; Ricci, D. *J. Phys. Chem.*, **1994**, *98*, 1620.

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