The Effect of Electrochemically Generated Positive Bromine Species in Acetonitrile on the Cleavage of C–Br and C–Cl Bonds

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The fate of bromine formed from C–Br cleavage during the course of anodic oxidation of alkyl bromides in acetonitrile on platinum has been investigated potentiostatically. It is suggested that positive bromine species are formed and they are potentially reactive towards alkyl bromides, yielding similar products to those obtained by direct anodic oxidation of the same bromides. Furthermore, whereas alkyl chlorides do not undergo C–Cl fission by direct anodic oxidation it is shown that positive bromine species are energetically sufficient to break C–Cl bonds, although not very efficiently. We suggest that a possible structure for the complex between acetonitrile and positive bromine species is mainly $[(CH_3CN)_2Br]^+Br_3^-$ or $[CH_3CNBr]^+Br_3^-$ and the mechanism for its formation is discussed. The spectrum of this species found identical to that of Br_3^- (269 nm) in acetonitrile.

It has been reported that anodic oxidation of acyclic [1] and cyclic [1c, 2] alkyl bromides (except for 2-bromoadamantane) gave exclusively carbon–bromine bond cleavage. While it is fairly well established that the organic fragments yield products derived from carbenium-ion type intermediates, the fate of the bromine is unknown. In fact, it is almost completely ignored or unreported. There is no mention in the literature of the detection of free Br_2 which could result from a recombination of bromine radicals. Not only that, as far as we know, there is no indication of any products derived from a radical reaction initiated by bromine atoms. For example, one would expect that in acetonitrile, succinonitrile would be formed (as a result of hydrogen abstraction from acetonitrile followed by dimerization).[3]

If no electrically neutral species is formed, presumably charged ones can be obtained under the conditions studied. There are two possible mechanisms by which charged species can form. (a) Bromine radicals undergo fast recombination at the electrode surface to form Br_2 which is immediately oxidized to Br_2^+. Should Br_2 be formed its immediate oxidation is expected since it is oxidized at a lower potential [4] (1.5 V *versus* Ag–Ag$^+$) than is applied for the oxidation of alkyl bromides (2.5 V). (b) Bromine radicals may undergo further oxidation at the electrode surface before recombination [reaction (1)].

$$Br^{\bullet}_{ads} \xrightarrow[CH_3CN]{anode} Br^+_{ads} \text{ or } [CH_3CNBr]^+ \qquad (1)$$

A chemically polarized oxidation from Br· to Br$^+$ at a platinum was previously proposed.[4b]

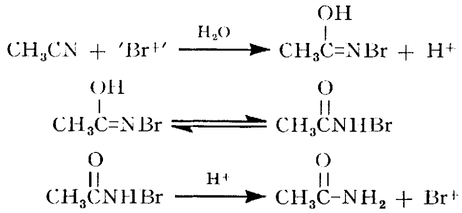
If indeed ionic species are formed in the cell, then one can reconcile the fact that no free Br_2 and no radical products have yet been detected.

This has encouraged us to initiate a systematic study of the cationic species possibly generated in the anodic cleavage of C–Br bonds. Since we do not know the exact nature of the as yet putative ionic species,† we will refer to it, hereafter, as ' Br$^+$.' The influence of such species on C–Br and C–Cl bond cleavage has also been studied.

RESULTS AND DISCUSSION

What kind of evidence can one gather to favour the postulate on an ionic bromine species being formed? There are both physical and chemical evidence implying the existence of ' Br$^+$ ' species. In the present study we observed a u.v. spectrum for an electrolysed solution of Br_2 in CH_3CN (AN) at 1.6 V (*versus* Ag–Ag$^+$) with $\lambda_{max.}$ 268 nm which is not derived from the solvent (210 nm), nor from Br_2 (418 nm).[6] This result indicates the possible formation of new species between Br_2 and AN.

Chemical evidence for ' Br$^+$ ' species was found when the AN used for the electrolysis of Br_2 was not dry enough and acetamide was observed after work-up. We suggest the mechanism in Scheme 1 as a possible explanation for the formation of acetamide in the presence of ' Br$^+$ ' species. Of course, it is also possible to assume the formation of acetamide by direct oxidation of the solvent. However, this possibility is unlikely since AN is electroinactive below *ca.* 2.5 V (Ag–Ag$^+$). This observation led us to pursue further the existence of the ' Br$^+$ ' species.



$$CH_3CN + \text{'}Br^+\text{'} \xrightarrow{H_2O} CH_3\overset{\overset{\displaystyle OH}{|}}{C}{=}NBr + H^+$$

$$CH_3\overset{\overset{\displaystyle OH}{|}}{C}{=}NBr \rightleftharpoons CH_3\overset{\overset{\displaystyle O}{||}}{C}NHBr$$

$$CH_3\overset{\overset{\displaystyle O}{||}}{C}NHBr \xrightarrow{H^+} CH_3\overset{\overset{\displaystyle O}{||}}{C}{-}NH_2 + Br^+$$

Scheme 1

Electrochemical Oxidation of Br_2 *in AN in the Presence of Alkyl Bromides.*—Others [2] as well as us,[1] have demonstrated that the breaking of C–Br bond can take place by direct anodic oxidation of bromoalkanes to yield *N*-alkylacetamides and olefins. Given the postulate of the existence of ' Br$^+$ ' in the anodic oxidation of bromo-

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† It is noteworthy that Br_2^+ is unlikely to be formed since it was found to be slightly stable even in superacid systems (*e.g.*, SbF_5–$2SO_3$–HSO_3F)[5] and to disproportionate to Br_3^+ and Br^+.

alkanes, is it possible that this species may intervene in the well established cleavage of the C–Br bond?

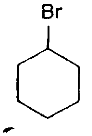
In order to study the reactivity of ' Br^+ ' species towards the C–Br bond, Br_2 was oxidized at 1.6 V in AN, in the presence of cyclohexyl bromide (1) which is oxidizable only above 2.5 V, under the conditions studied. We have studied the effect of electrolysed solutions with various [(1)] : [Br_2] ratios, on the scission of the C–Br bond. The results are summarized in Table 1. The chemical efficiency of the cleavage increases as the above ratio decreases. As a result of C–Br cleavage, *N*-cyclohexylacetamide (2) and cyclohexene, which was trapped as 1,2-dibromocyclohexane (3), were formed, as in the direct electro-oxidation of bromocycloalkanes.[1c]

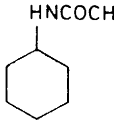
TABLE 1

The effect of electrogenerated positive bromine species on various relative concentrations of bromocyclohexane [a]

[(1)]/[Br_2]	Total mF consumed	F per mole Br_2	Yield of (2) [mmol (%)] [b]	Yield of (3) [mmol (%)] [c]	Reaction time (h)
0.5/4.0 = 0.12	31.90	0.53	0.480 (6.4)	0.075 (1.0)	8.0
0.5/2.35 = 0.21	9.41	0.40	0.590 (11.8)	0.030 (0.6)	4.5
0.5/1.95 = 0.25 [d]	2.50	0.06	0.075	0.008 (0.2)	5.0
0.5/1.5 = 0.34	11.42	0.51	0.480 (6.4)	0.046 (0.6)	6.0
0.5/0.975 = 0.51	4.55	0.47	0.280 (5.6)	0.024 (0.5)	4.0
0.5/0.5 = 1.0	2.43	0.33	0.140 (1.9)	0.024 (0.3)	6.0
0.5/0.325 = 1.54	4.93	0.51	0.260 (1.7)	0.027 (0.2)	7.0
0.5/0.245 = 2.0	2.18	0.45	0.250 (2.5)	0.011 (0.2)	6.0
0.5/0.1 = 5.0	0.86	0.57	0.032 (0.4)	0.014 (0.2)	4.0
0.5/0.1 = 5.0	3.01	2.00	0.160 (2.2)	0.029 (0.4)	4.0

[a] Experimental conditions: controlled potential at 1.6 V (*versus* Ag—0.1N-$AgNO_3$) in CH_3CN–0.1N-$LiClO_4$ under nitrogen at 38 ± 1 °C. Initial currents were in the range 50—100 mA which decreased to 5—15 mA when the reaction stopped. [b] Yields are based on calibration curves employing g.l.c. [c] Yields are based on calibration curves. [d] At 20 °C ± 1.


(1)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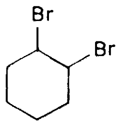

(3)

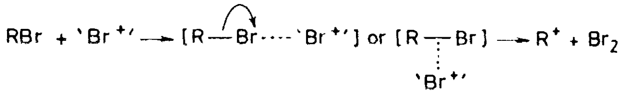
TABLE 2

The effect of electrogenerated positive bromine species on various alkyl bromides [a]

Substrate (M)	Br_2 (M)	Total mF consumed	F per mole Br_2	Reaction time (h)	Products (%) [b]
Cyclohexyl bromide (0.5)	0.3	4.93	0.51	5.0	*N*-Cyclohexylacetamide (10) 1,2-Dibromocyclohexane (1) 3-Acetamidocyclohexene (2)
Cyclopentyl bromide (0.53)	0.27	2.05	0.51	4.0	*N*-Cyclopentylacetamide (14) 1,2-Dibromocyclopentane (1)
Cycloheptyl bromide (0.53)	0.27	2.76	0.69	2.0	*N*-Cycloheptylacetamide (13) 1,2-Dibromocycloheptane (1)
Isopropyl bromide (0.53)	0.27	1.61	0.41	7.0	Isopropylacetamide (8)
s-Butyl bromide (0.53)	0.27	2.05	0.51	5.0	2-Acetamidobutane (10) t-Butylacetamide (trace) 1-Acetamidobutane (trace)
1-Bromo-2-methylpropane (0.53)	0.27	4.18	0.91	3.5	t-Butylacetamide (32) 1-Acetamido-2-methylpropane (trace)
1-Bromobutane (0.53)	0.27	2.97	0.37	8.0	2-Acetamidobutane (trace) 1-Acetamidobutane (trace)
2-Bromopentane (0.53)	0.53	3.10	0.38	5.0	2-Acetamidopentane (10)

[a] Experimental conditions: acetonitrile–0.1M-$LiClO_4$ (15 ml); nitrogen atmosphere; controlled potential at 1.6 V *versus* Ag–0.1N-$AgNO_3$ and at 38 ± 1 °C. [b] Identification of products by authentic samples and g.l.c.–m.s. Yields of all amides and dibromides are based on calibration curves of (2) and (3), respectively; therefore, yields of products other than (2) and (3) are approximate.

The cleavage of C–Br by ' Br^+ ' can be initiated by an S_E2 type mechanism or by a central attack on the bond (with no intention to imply the preference of either mechanism) (Scheme 2).



SCHEME 2

Table 2 summarizes the results obtained by reacting ' Br^+ ' with a variety of alkyl bromides. As expected, cleavage is favoured for secondary bromides over primary ones. However, when a rearrangement to a more stable carbocation is possible, as in the case of 1-bromo-2-methylpropane, the cleavage process is even more efficient (32%) compared with the average total yield from each reaction (*ca.* 15%). The results, in general, indicate that ' Br^+ ' species possess enough energy to break the C–Br bond, but the reaction is not so efficient. For comparison, the more efficient (40—75% yield) direct anodic cleavage of C–Br bond requires higher potentials (>2.5 V). It is clear now that organic fragments derived from the electro-oxidation of alkyl bromides can also be formed *via* reaction with ' Br^+ ', although not as efficiently as in the direct oxidation.

The Polar Nature of $Br_2 + AN$ *Solution and its Influence on* C–Br *Bond Breaking*.—The question now arises whether the origins of ' Br^+ ' in our reaction mixture is exclusively anodic. It is known [7] that although Br_2 has a low dielectric constant (3.09) its mixtures with acetamide, pyridine, quinoline, acetonitrile, and diethyl ether show a relatively high conductivity. For example, the equivalent conductivity of pyridine–Br_2 (1M) in nitrobenzene is 7.11 Ω^{-1} cm^2 equiv^{-1} compared with that of acetic acid (0.1M) in water, which is only 4.67 Ω^{-1} cm^2 equiv^{-1}.[7,8] The explanation for this is based on the assumption that ionic complexes are formed which behave as weak electrolytes in aprotic media, for example equations (2) or (3).

$$\text{pyridine}\cdot 2Br_2 \rightleftharpoons [C_5H_5N\cdot Br]^+ + Br_3^- \qquad (2)$$

$$CH_3CONH_2\cdot Br_2 \rightleftharpoons [CH_3CONH_2Br]^+ + Br^- \qquad (3)$$

Popov *et al.*[9] postulated that a charge transfer complex is formed from acetonitrile and halogens. A 1 : 1 complex was suggested for CH_3CN–ICl, CH_3CN–IBr, and CH_3CN–I_2 mixtures.[7-9] The formation of this charged species were explained by Mülliken [10] as in Scheme 3. This mechanism suggests two charged complexes, an 'outer complex' ($CH_3CN\cdot X_2$) and an 'inner complex' ($CH_3CNX^+X^-$), which are interconvertable. The latter, if indeed present, could be due to a spontaneous chemical reaction, and does not involve anodic oxidation.

It is also possible that two acetonitrile molecules are co-ordinated to the positive bromine and the last two reactions in Scheme 3 may be replaced by each of

$$\begin{aligned} CH_3CN + X_2 &\rightleftharpoons CH_3CN\cdot X_2 && \text{(fast)} \\ CH_3CN\cdot X_2 &\rightleftharpoons CH_3CNX^+X^- && \text{(slow)} \\ CH_3CNX^+X^- &\rightleftharpoons [CH_3CNX]^+ + X^- && \text{(fast)} \\ X_2 + X^- &\rightleftharpoons X_3^- && \text{(fast)} \end{aligned}$$

SCHEME 3

equations (4) and (5); the first is in analogy to the mechanism suggested for pyridine·ICl.[11] Does this scheme also apply to our case?

$$2CH_3CNX^+X^- \rightleftharpoons [(CH_3CN)_2X]^+ + X_3^- \qquad (4)$$

$$CH_3CNX^+X^- + X_2 \rightleftharpoons [CH_3CNX]^+ + X_3^- \qquad (5)$$

On the basis of the known absorption spectra recorded for Me_4NBr in acetonitrile [$\lambda_{max.}(Br^-)$ 218 nm (ε 10^4)] [12] and Bu_4NBr_3 in the same solvent [$\lambda_{max.}(Br_3^-)$ 269 nm (ε 55 000)],[13] and our u.v. results (see before) we suggest that $Br_2 + CH_3CN$ forms a complex analogous to the one discussed in the mechanistic scheme, and whose structure is $[(CH_3CN)_2Br]^+Br_3^-$ or $[CH_3CNBr]^+Br_3^-$.*

Making the reasonable assumption that Bu_4NBr_3 is completely dissociated in CH_3CN, one may calculate the extent of dissociation of the complex formed in our experiments. A solution of Br_2 ([Br_2] 3×10^{-5}M) in acetonitrile gives an optical density of 0.6. From the known molar extinction of Br_3^-, the concentration of 'free' Br_3^- in this solution should be 1.09×10^{-5}M (optical path length 1 cm). Since a 3.0×10^{-5}M solution of Br_2 could give a maximum Br_3^- concentration of 1.5×10^{-5}M, the yield of free (dissociated) Br_3^- is *ca.* 73%. In this simple calculation we assume that the cation of the complex and any other positive bromine species do not contribute to the absorption at 269 nm. This assumption is quite reasonable since the known u.v. spectra of Br_2^+ and Br_3^+ in superacid media was reported to be $\lambda_{max.}$ 510 (ε 1 400) and 375 nm (1 600), respectively.[5]

If indeed Br_2 in AN forms ' Br^+,' then the so-formed species can partake in C–Br bond cleavage.

To examine the influence of $AN + Br_2$ solutions on C–Br bond we carried out experiments with various [(1)]/[Br_2] ratios without electrolysing the solutions. The results, which are described in Table 3, show that products due to C–Br bond rupture were formed only when [(1)]/[Br_2] < 1, but even then, at very low yields. This result indicates that ' Br^+ ' species are indeed present but in low concentration owing to 'poor ionization' of the acetonitrile–bromine complex. In fact, it is so poor that the concentration of free ' Br^+ ' is minute. An analogy to this behaviour does exist; it was previously shown that other acetonitrile–halogen complexes behave similarly.[9] It was also stated that it appears to be extremely unlikely that in iodoacetonitrile, for instance, the iodine would be sufficiently positive to be titratable iodometrically.[9]

TABLE 3

The effect of non-electrolysed solutions of Br_2 in AN in the presence of bromocyclohexane [a]

(1)/[Br_2]	(2) (%)	(3) (%)	Reaction time (h)
0.5/2.0 = 0.25	14.0	3.0	24
0.5/2.0 = 0.25	0.3	0.2	6
0.5/0.5 = 1.0	Trace	Trace	6
0.5/0.25 = 2.0	Trace		16
0.5/1.0 = 0.5			16
0.5/0.5 = 1.0 [b]	Trace	Trace	5

[a] Experimental conditions as in Table 2. [b] Without the presence of $LiClO_4$.

The fact that ionization is poor does not preclude the presence of some concentration of ' Br^+ ' which could partake in C–Br bond breaking. Indeed, when we allowed the non-electrolysed solutions to stand for longer periods (first entry in Table 3) the yield of C–Br bond cleavage derived products, increased. This trend was found to be true for compound (1) as well as for other bromoalkanes listed in Table 4. Tertiary bromides gave quite high yields. In order to exclude the intervention of the non-electrochemical reaction we have limited the

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* Under certain concentration conditions, a u.v. absorption corresponding to Br^- has also been observed. This cannot exclude the possibility that it may serve partly as a counterion in the complex. In addition to Br_3^- and Br^-, ClO_4^- may also act as a counterion in the electrolysed mixture.

investigation to primary and secondary alkyl bromides and to relatively short periods (Table 2), where this reaction is inefficient.

The conclusive result that the products yield is higher in the presence of electrochemically generated ' Br$^+$ ' than in non-electrolysed solutions of Br$_2$ is in agreement with the mechanism described in Scheme 3 for the slow conversion of ' outer ' to ' inner ' complex. Presumably, in our case, the ' inner ' complex is generated directly by the anodic process and not *via* the ' outer ' complex. This means that the rate-determining step, $AN{\cdot}Br_2 \rightleftharpoons ANBr^+Br^-$, is being skipped and consequently a higher concentration of ' Br$^+$ ' is present in the solution.

In conclusion, C–Br bond scission in the anodic oxidation of alkyl bromides occurs by two different pathways, one by a direct electrochemical process and the second, indirectly, *via* electrochemically generated positive bromine species. The latter pathway is less efficient than the former but can take place at lower potential.

Electrochemical Oxidation of Br$_2$ *in AN in the Presence of Alkyl Chlorides*.—There is no precedent in the literature for direct anodic oxidation of the C–Cl bond. In fact, electro-oxidation of 1-chloroadamanate leads exclusively to C–H bond cleavage and to products which contain chlorine atoms.[2b,d]

The ability of electrochemically generated ' Br$^+$ ' species to cleave C–Cl bonds was studied. The results are described in Table 5. The C–Cl bond can be cleaved indirectly although the efficiency of the process is lower than for C–Br, as expected, since the C–Cl bond is stronger than the C–Br bond.

TABLE 4

The effect of non-electrolysed solutions of Br$_2$ in AN on primary, secondary, and tertiary aliphatic bromides [a]

Substrate (M)	Br$_2$ (M)	Reaction time (h)	Products (%) [b]
Cyclohexyl bromide (0.2)	0.8	5	*N*-Cyclohexylacetamide (1) 1,2-Dibromocyclohexane (Trace)
Cyclohexyl bromide (0.2)	0.8	24	*N*-Cyclohexylacetamide (14) 1,2-Dibromocyclohexane (3)
Cyclohexyl bromide (0.32)	0.16	24	No product
Cyclopentyl bromide (0.2)	0.8	6	*N*-Cyclopentylacetamide (1.5) 1,2-Dibromocyclopentane (Trace)
Cyclopentyl bromide (0.2)	0.8	24	*N*-Cyclopentylacetamide (13) 1,2-Dibromocyclopentane (1.8)
Cycloheptyl bromide (0.2)	0.8	5	*N*-Cycloheptylacetamide (0.5) 1,2-Dibromocycloheptane (Trace)
Cycloheptyl bromide (0.2)	0.8	24	*N*-Cycloheptylacetamide (14) 1,2-Dibromocycloheptane (2)
Isopropyl bromide (0.2)	0.8	6	Isopropylacetamide (Trace)
Isopropyl bromide (0.2)	0.8	24	Isopropylacetamide (1)
1-Bromo-2-methylpropane (0.2)	0.8	5	t-Butylacetamide (Trace)
1-Bromo-2-methylpropane (0.2)	0.8	24	t-Butylacetamide (1)
s-Butyl bromide (0.2)	0.8	6	s-Butylacetamide (Trace)
s-Butyl bromide (0.2)	0.8	24	s-Butylacetamide (Trace)
1-Bromoadamantane (0.2)	0.8	24	1-Acetamidoadamantane (48)
1-Bromoadamantane (0.32)	0.16	24	1-Acetamidoadamantane (10)
t-Butyl bromide (0.2)	0.8	24	t-Butylacetamide (9)
t-Butyl bromide (0.32)	0.16	24	t-Butylacetamide (4)
1-Bromobutane (0.2)	0.8	24	s-Butylacetamide (Trace) 1-Acetamidobutane (Trace)
2-Bromopentane (0.2)	0.8	24	2-Acetamidopentane (trace)

[a] Experimental conditions as in Table 2 except for using a volume of 25 ml for all solutions. [b] As described in footnote *b* in Table 2.

TABLE 5

The effect of electrogenerated positive bromine species relative to non-electrolysed solutions of Br$_2$ + AN on the C–Cl bond of various chloroalkanes [a]

Substrate (M)	Br$_2$ (M)	Reaction time (h)	Total mF consumed	F per mole Br$_2$	Products (%) [b]
Cyclohexyl chloride (0.2)	0.8	24			No product
Cyclohexyl chloride (0.33)	1.33	4	10	0.5	*N*-Cyclohexylacetamide (8.6) 1,2-Dibromocyclohexane (Trace) 3-Acetamidocyclohexene (1)
s-Butyl chloride (0.2)	0.8	6			No product
s-Butyl chloride (0.32)	0.16	24			No product
s-Butyl chloride (0.33)	1.33	7	1.65	0.4	2-Acetamidobutane (7) 1-Acetamidobutane (Trace)
t-Butyl chloride (0.2)	0.8	24			t-Butylacetamide (7)
t-Butyl chloride (0.32)	0.16	24			t-Butylacetamide (2)
t-Butyl chloride (0.53)	0.27	0.5	2.41	0.6	t-Butylacetamide (22.5)
1-Chloropropane [c] (0.56)	1.35	8	3.9	0.14 [d]	1-Acetamidopropane (Trace)

[a] See footnote *a* in Table 2. [b] See footnote *b* in Table 2. [c] At 20 ± 1 °C. [d] The current throughout electrolysis was just above the background value.

EXPERIMENTAL

Electrolyses.—Materials, instrumentation, cyclic voltammetry measurements, and preparative oxidations of alicyclic bromides were previously described.[1c] In a typical experiment for oxidizing bromine solutions, acetonitrile–0.1M-$LiClO_4$ solution (15 ml) was introduced into the anodic compartment and the same solution was introduced into the cathodic part until they reached the same level. Then bromocyclopentane (8 mmol) and Br_2 (4 mmol) were added to the anolyte solution and an additional portion of the solvent–electrolyte solution was added to the catholyte to level up the solutions. The electrochemical cell was immersed in a warm water-bath (*ca.* 38°) and the solution was flushed with nitrogen throughout the electrolysis. The potential was fixed to 1.6 V (*versus* Ag–0.1N-$AgNO_3$) and initial current was 50—60 mA. After passing 2mF the electrolysis was stopped and the anolyte solution was evaporated to *ca.* 5 ml. Then a 10% $NaHSO_3$ solution was added until the brown colour disappeared. The solution was extracted three times into $CHCl_3$ or CH_2Cl_2, the organic phase was washed with water, dried ($MgSO_4$), and concentrated. The mixture was analysed by g.l.c., using a 2 m × $\frac{1}{4}$ in 10% SE–30 column and the products were compared with authentic samples.

In parallel to the electrolyses, controlled blank experiments were done. Various compositions of the anolyte mixtures were allowed to stand for 4—24 h at *ca.* 38 °C under an inert atmosphere and then treated as described for the controlled potential electrolysis.

U.v. Measurements.—A known concentration of Br_2 in CH_2Cl_2 (100 ml) was prepared. Several concentrations of CH_3CN in CH_2Cl_2 (10 ml) were prepared. Before each measurement, 0.1 ml of the bromine solution was introduced into each CH_3CN–CH_2Cl_2 mixture and the spectrum was recorded in the region 200—400 nm.

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REFERENCES

[1] (*a*) J. Y. Becker and M. Münster, *Tetrahedron Letters*, 1977, 455; (*b*) J. Y. Becker, *J. Org. Chem.*, 1977, **42**, 3997; (*c*) J. Y. Becker and D. Zemach, *J.C.S. Perkin II*, 1979, 914.

[2] F. Vincent, R. Tardivel, and P. Mison, (*a*) *Tetrahedron Letters*, 1975, 603; (*b*) *Tetrahedron*, 1976, **32**, 1681; V. R. Koch and L. L. Miller, (*c*) *J. Amer. Chem. Soc.*, 1973, **95**, 8631; (*d*) *Tetrahedron Letters*, 1973, 693.

[3] H. Schmidt and J. Noack, *Z. Anorg. Allgem. Chem.*, 1958, **296**, 262; F. Vincent, R. Tardivel, and P. Mison, *Tetrahedron*, 1976, **32**, 1681.

[4] (*a*) G. Casalbore, M. Mastrogostino, and S. Valcher, *J. Electroanalyt. Chem.*, 1978, **87**, 411; 1977, **77**, 373; (*b*) F. Mango, G. A. Mazzocchin, and G. Bontempelli, *ibid.*, 1973, **47**, 461.

[5] R. J. Gillespie and M. J. Morton, *Inorg. Chem.*, 1972, **11**, 586.

[6] J. P. Simons, ' Photochemistry and Spectroscopy ', Wiley-Interscience, Wiley, New York, 1971, pp. 260—270.

[7] E. Ya. Gorenbein and A. E. Gorenbein, *Russ. J. Inorg. Chem.*, 1967, **12**, 954.

[8] I. Rubinstein, M. Bixon, and E. Gileadi, *J. Phys. Chem.*, 1980, **84**, 715.

[9] A. I. Popov and W. A. Deskin, *J. Amer. Chem. Soc.*, 1958, **80**, 2976.

[10] R. S. Mülliken, *J. Phys. Chem.*, 1952, **56**, 801.

[11] A. I. Popov and R. T. Pflaum, *J. Amer. Chem. Soc.*, 1957, **79**, 570.

[12] J. Jortner and A. Treinin, *Trans. Faraday Soc.*, 1962, **58**, 1503.

[13] A. I. Popov and R. F. Swensen, *J. Amer. Chem. Soc.*, 1955, **77**, 3724.