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## Oxidation of Cyclic Hydrocarbons by Cobalt(III) Acetate

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The oxidation of cyclic alkanes and alkenes by cobalt(III) acetate leads to the formation of cycloalkyl and cycloalkenyl acetates. The formation of chlorinated hydrocarbons is observed for cycloalkanes in the presence of carbon tetrachloride but no incorporation of chlorine takes place in the olefins. The results are best interpreted by assuming a determining role by both steric and conformational effects on the reaction, involving the conversion of a coordinated radical to a carbocation.

THE oxidation of hydrocarbons with cobalt(III) acetate has been thoroughly investigated recently.<sup>1-5</sup> Unexpected selectivities have been observed,<sup>3</sup> and much information on the mechanism of the reaction has been obtained from kinetic determinations on aralkyl hydrocarbons.<sup>4,5</sup> As far as selectivity is concerned, the most striking features have been observed for the alkane series where preferential attack on a methylene group in position 2 was detected in the case of linear hydrocarbons even when a tertiary C-H bond is present. *E.g.* in the case of 2-methylpentane, position 4 is selectively substituted.<sup>3</sup>

The results have been interpreted as a balance between hyperconjugative and steric effects, the 2-position of a linear hydrocarbon being more prone to give species stabilized by no-bond resonance than any other position, whereas increasing substitution of this position makes it more sterically hindered, thereby cancelling any gain in inductive stabilisation. On the other hand, cycloalkanes, olefins, and particularly cycloalkenes have not yet been fully investigated. We now report our observations for these latter species. We hoped that, as the reaction is extremely sensitive to both steric and electronic effects,<sup>3-5</sup> the use of cyclic hydrocarbons as substrates would give information on the role of ring conformation.

TABLE I

Oxidation of adamantane and norbornane			
Acetoxylation experiments: [hydrocarbon] 0.5M; [Co <sup>III</sup> ] 0.5M; [TFA] 1M; acetic acid 35 ml			
Chlorination experiments: [hydrocarbon] 0.5M; [Co <sup>III</sup> ] 0.5M; [CCl <sub>4</sub> ] 4M; no TFA; acetic acid 35 ml; 40°; 24 h.			
Acetoxylation		Chlorination	
Products	Yield (%)	Products	Yield (%)
Adamantane (A)	13	Adamantane	10
Adamantanols (B)	(15)	1-Chloroadamantane	39.5
1-Adamantyl acetate (C)	48	2-Chloroadamantane	2.5
1,3-Diacetoxyadamantane (D)	9	1,3-Dichloroadamantane	11.0
High boiling material (E) (triacetate ?)	(17)		

\* In mole % except for values in parentheses (unidentified compounds) which are calculated in w/w %.

## RESULTS

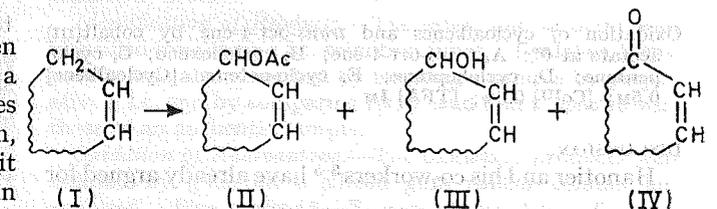
The behaviour of cyclic hydrocarbons is drastically different from the previously studied open-chain compounds.<sup>3</sup>

<sup>1</sup> R. A. Sheldon and J. K. Kochi, *Oxidation and Combustion Rev.*, 1973, **5**, 135, and references therein.

<sup>2</sup> E. I. Heiba, R. M. Dessau, and W. J. Koehl, jun., *J. Amer. Chem. Soc.*, 1969, **91**, 6830.

<sup>3</sup> J. Hanotier, Ph. Camerman, M. Hanotier-Bridoux, and P. de Radzitzky, *J.C.S. Perkin II*, 1972, 2247.

As opposed to linear alkanes, cyclohexane gives a surprisingly small yield of oxidation product (3–5% of cyclohexyl acetate together with traces of cyclohexanol and cyclohexanone). However oxidation in the presence of carbon tetrachloride<sup>3</sup> gives higher yields than acetoxylation, 30% chlorocyclohexane being obtained. Much higher yields are obtained from norbornane [(norbornyl acetate 20%) and adamantane [total yield of esters 80% (Table I)] than from cyclohexane. Acetoxylation as well as chlorination of adamantane takes place selectively on the tertiary carbon



atoms in contrast to the oxidation of 2-methylpentane which is attacked at the 4-position.<sup>3</sup> The lack of steric hindrance at the tertiary carbon atoms of adamantane is probably the main factor which explains the observed selectivities.

The oxidation of cycloalkenes by cobalt(III) acetate leads to the formation of allylic acetates, together with traces of alcohols and ketones. The yields are good (Table 2) and the reaction is very fast at 40°. Therefore the kinetic measurements were performed at 0° and the results are reported in the Figure. Notable differences are observed among the olefins investigated, *e.g.* cyclohexene is oxidized faster than its homologues and its reactivity approaches the behaviour of a linear olefin such as *trans*-oct-4-ene (Figure) and may be considered therefore as more 'normal'.

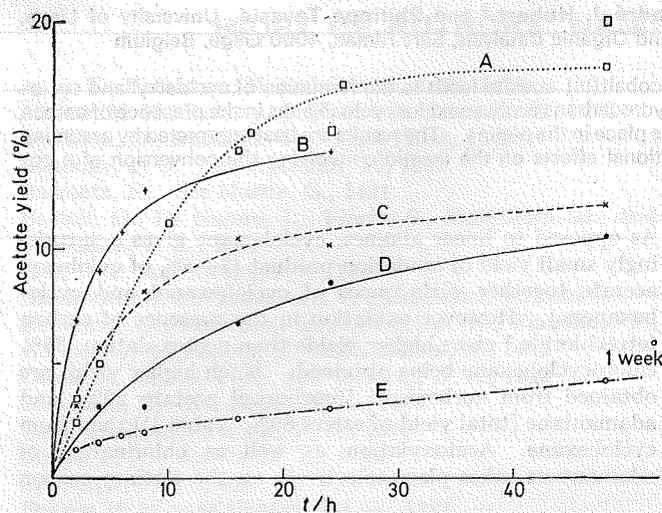
The better yield of cyclohex-2-enyl acetate by contrast with the corresponding esters from homologous olefins can be related to little interference by side reactions leading to the unproductive consumption of cobalt(III). This is demonstrated by the slow decrease of Co<sup>III</sup> in the absence of substrate and by comparing the oxidation of cyclohexene in the presence of an excess of substrate to the oxidation of the same olefin in the presence of an excess of Co<sup>III</sup> (Table 3). Unchanged olefin is recovered even in the latter case [after complete reduction of cobalt(III)].

By-products can be detected in some cases, *e.g.* cyclohex-2-enol is formed in 4% yield at 0° and higher temperatures. Traces of cyclopent-2-enol and cyclopent-2-one (respectively 0.2 and 0.4%) are detected after only 24 h in the case of cyclopentene (at 40° formation of cyclopentadiene from

<sup>4</sup> J. Hanotier, M. Hanotier-Bridoux, and P. de Radzitzky, *J.C.S. Perkin II*, 1973, 381.

<sup>5</sup> J. Hanotier and M. Hanotier-Bridoux, *J.C.S. Perkin II*, 1973, 1035.

cyclopent-2-enyl acetate requires long reaction times), whereas no alcohols nor ketones at all are observed with the other olefins investigated.



Oxidation of cycloalkenes and *trans*-oct-4-ene by cobalt(III) acetate at 0°: A, *trans*-oct-4-ene; B, cyclohexene; C, cyclopentene; D, cycloheptene; E, cyclo-octene. [Cycloalkene] 0.5M; [Co<sup>III</sup>] 0.5M; [TFA] 1M

#### DISCUSSION

Hanotier and his co-workers<sup>3-5</sup> have already argued for

appreciable differences of reactivities between the homologous cycloalkenes (Figure). The use of models for five-, six-, seven-, and eight-membered cyclic carbenium ions predicts a particularly favourable conformation for the six-membered ring. Moreover in opposition to the two lower members of the series which have a rather flat structure, the C<sub>7</sub> and C<sub>8</sub> cyclic ions have U-shaped conformations which are, on one side of the ion at least, convenient for co-ordination and are not suitable for subsequent approach of the counterion from the opposite side.

The curves obtained at 0° show a sharp decrease of the rate of oxidation after the initial stage and the yields are at most half of those observed at 40° (Table 2). This phenomenon may be tentatively interpreted by a stabilization of inactive Co<sup>II</sup>-Co<sup>III</sup><sup>3</sup> aggregates at low temperature even in the presence of trifluoroacetic acid (TFA). Moreover the unfavourable conformations have an increasingly inhibiting effect upon lowering the temperature as interconversions become progressively 'frozen'.

The oxidation of adamantane brings additional support to the hypothesis that the reaction is very sensitive to steric hindrance. The observed selectivities could possibly be interpreted by an ionic mechanism<sup>6</sup> but this is in contradiction to published work.<sup>3</sup>

Our results are best explained by a mechanism similar to that (Scheme) proposed by Hanotier and his co-

TABLE 2

Oxidation of cycloalkenes at 40° [Olefin] 0.5M; [Co<sup>III</sup>] 0.5M; [TFA] 1.0M

t/h	Cyclopentene			Cyclohexene*				Cycloheptene				Cyclo-octene				
	0.25	1	24	0.25	1	4	24	1	3	8	24	1	3	8	24	170
Cycloalkene (%)		(53) <sup>a</sup>	(57) <sup>b</sup>	66	68	58	60	88	90	75	80	81	83	79	72	76
Cycloalk-2-enyl acetate (%)	11.7 <sup>b</sup>	11.3 <sup>a</sup>	4.3 <sup>a</sup>	24	30	37	44	16	19	21	22	18	22	23	23	23
Cycloalk-2-enyl alcohol (%)	0	0	0.2	7	3	5	4	0	0	0	0	0	0	0	0	0
Co <sup>III</sup> (%)	5.65	0	0	32	24	15	0	32	6	1	0	28	4.6	0.9	0	0

Yields are given in mole %.

<sup>a</sup> Values in parentheses are low as some cyclopentene was lost during the analytical process because of its volatility. <sup>b</sup> Cyclopentadiene was slowly formed from cyclopent-2-enyl acetate (6% after 24 h). Cyclopent-2-enone was observed with cyclopentene (respectively 1.6, 1.6, and 0.4% after 1, 4, and 24 h) together with some unidentified material (0.3, 1.0, and 6.1%).

\* Cyclohexyl acetate was detected in 1% yield. It was formed by addition of acetic acid on the double bond in the presence of TFA.

TABLE 3

Oxidation of cyclohexene at 40°

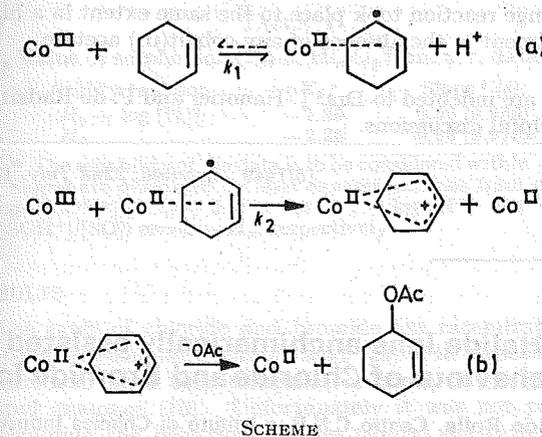
t/h	[olefin] 0.5M; [Co <sup>III</sup> ] 0.5M; [TFA] 1M				[olefin] 0.5M; [Co <sup>III</sup> ] 1.5M; [TFA] 3M				
	[Co <sup>III</sup> ] (%)	Cyclohexene (%)	Cyclohex-2-enyl acetate (%)	Cyclohex-2-enyl alcohol (%)	t/h	[Co <sup>III</sup> ] (%)	Cyclohexene (%)	Cyclohex-2-enyl acetate (%)	Cyclohex-2-enyl alcohol (%)
0.25	37	66	24	7	0.25	84	62.5	27.0	8
1.0	34	68	30	3	0.5	71	73.8	27.5	11
4.0	16	58	37	5	1.0	60	57.5	35.0	10.5
24	0	60	44	4	2.0	44	48.3	41.0	9.4
					4.0	25	46.0	47.5	9.4
					8.0	17	34.0	54.0	10
					16		28.0	64.0	7
					24	1.2	37.0	61.3	5.5

the importance of steric and hyperconjugative effects in explaining the observed selectivities during the oxidation of linear hydrocarbons. In our case, the influence of conformational effects can be invoked to explain the

workers for the oxidation of aralkyl hydrocarbons.<sup>2,4,5</sup> Oxidation experiments in DOAc as solvent do not show

<sup>6</sup> I. Tabushi, Z. Yoshida, and Y. Tamaru, *Tetrahedron Letters* 1973, 29, 81.

any significant incorporation of deuterium in the substrates. Therefore step (a) is *not* a fast equilibrium, as already suggested by the fact that  $k_2$  is not negligible compared with  $k_1$  in the rate equation reported by Hanotier and his co-workers.<sup>3</sup> Unlike the case for alkanes however, the formation of a radical intermediate in step



SCHEME

(a) cannot be demonstrated in the case of olefins by adding a chlorine-donating reagent (CCl<sub>4</sub>) as no chlorinated products are formed at all. Resonance stabilization of the intermediate radical may explain its lack of reactivity for such abstraction reactions. The relatively good yield of chlorocyclohexane in the presence of CCl<sub>4</sub>, particularly in regard to the small yield of acetoxyated product, can be accounted for by the sluggish formation of a cationic intermediate from the radical.

It is therefore obvious that a co-ordination mechanism offers a logical explanation for the large changes in selectivity observed in the oxidation of sterically hindered compounds. The co-ordination of the intermediate radical by Co<sup>II</sup> ion is in agreement with Hanotier's results and also explains our observations. We also stress however that, in step (a), the cleavage of a C-H bond takes place at low temperature. The nature of the necessary initial interaction remains obscure mainly in the case of alkanes although recent observations have been reported on such effects.<sup>7</sup>

**Conclusions.**—From these results, it appears that cobalt(III) acetate is efficient for the preparation of alk-2-enyl acetates from olefins, as well as for the acetoxylation of alkanes or arylalkanes. It is not effective however with cyclohexane. The yields and rates of the reactions are very sensitive to both electronic and steric effects, but our results show the predominance of both conformational and steric effects on the course of the reaction. A co-ordination mechanism which implies an intermediate radical, co-ordinated to Co<sup>II</sup>, best rationalizes these observations.

#### EXPERIMENTAL

**Starting Materials.**—The cycloalkanes, adamantane, and the olefins were commercial products and their purity

<sup>7</sup> C. Masters, *J.C.S. Chem. Comm.*, 1973, 191.

<sup>8</sup> A. C. Udding, J. Strating, H. Wynberg, *Tetrahedron Letters*, 1968, 1345.

(>99%) was checked by g.l.c. Cobalt(III) acetate was prepared according to the reported procedure.<sup>3</sup>

**Kinetics.**—The rate of reduction of cobalt(III) acetate was followed by titrimetry. A portion of the solution was poured into an excess of a Mohr's salt solution (0.15N). The excess of iron(II) was titrated in acid solution against a solution of potassium dichromate (0.3N).

The rate of formation of the oxidation products and the concentration of starting material was measured by g.l.c. [Intersmat ICG 15; flame ionisation detector; Carbowax 1540 (20%) on Celite 60-80; 15 ft × 1/8 in; 10° min; mesitylene as internal standard]. The reproducibility of the measurements performed with different batches of Co<sup>III</sup> was not good, and the results were checked by oxidizing cyclohexene as a standard in every series of experiments. In many cases, the measurements of the concentration of hydrocarbons (mainly the more volatile ones) were not very accurate, mainly because of solvent interference with the peaks of the starting material, and loss of this material. In such cases, the reaction was referred to a blank experiment in which the starting material was treated exactly as the reacting solution, but in the absence of cobalt(III) acetate.

**Identification of Products.**—The esters and alcohols were identified from their g.l.c. retention times. Cyclohex-2-enyl acetate was also identified by isolating a sample by preparative g.l.c. and by comparing its i.r. and n.m.r. spectra with those of an authentic sample.

**Oxidation of Adamantane.**—The oxidation products were isolated by g.l.c. on a silicon gum rubber column and analysed. Five peaks (A-E) were observed (see Table 1).

The i.r. spectrum showed the typical absorptions for an ester group at 1710 and 1315 cm<sup>-1</sup> in the case of C-E. The n.m.r. spectra indicated the preferred substitution of the tertiary CH proton in C and D as no absorption took place in the δ 4.85 region which was typical for the CHOAc group.<sup>8</sup> A fraction consisted mainly of unchanged adamantane, whereas C and D were respectively 1-adamantyl acetate, m.p. 30-33° (lit.<sup>9</sup> 33-34°) (Found: C, 74.0; H, 9.3; O, 16.5. Calc. for C<sub>12</sub>H<sub>18</sub>O<sub>2</sub>: C, 74.2; H, 9.3; O, 16.5%), *m/e* 194 (M<sup>+</sup>), and 1,3-diacetoxyadamantane (Found: C, 66.7; H, 8.5. Calc. for C<sub>14</sub>H<sub>20</sub>O<sub>4</sub>: C, 66.6; H, 8.0%). Fraction E could not be analysed but the i.r. spectrum suggested it was a polyacetate (triacetate?). Fraction B contains isomeric adamantanol, *m/e* 152 (M<sup>+</sup>), which could not be obtained sufficiently pure to allow satisfactory spectroscopic studies and analysis.

**Chlorination Experiments.**—The chlorination of cyclohexane and of adamantane was performed under the same conditions as acetoxylation without TFA, but in the presence of CCl<sub>4</sub> (4M). Chlorocyclohexane and chloro-adamantane were identified by g.l.c. by comparison with authentic samples (in the case of adamantane, they were prepared according to ref. 6); 1-chloro-adamantane and 1,3-dichloro-adamantane were also identified by i.r., mass, and n.m.r. spectroscopy after isolation by preparative g.l.c. on a silicon gum rubber column. The lack of any absorption in the n.m.r. spectra of both products at δ 4.13,<sup>10</sup> typical of the CHCl group, allowed identification of the 1-substituted product; similarly the existence of this absorption confirmed the presence of the 2-isomer. The mass spectrum (70 eV)

<sup>9</sup> F. N. Stepanov and Z. E. Stolyarov, *Zhur. Vsesoyuz. Khim. obsch.*, 1968, 13, 713.

<sup>10</sup> W. Hoeck, J. Strating, and H. Wynberg, *Rec. Trav. chim.*, 1966, 85, 1045.

of 1-chloroadamantane showed peaks at *m/e* 170 and 172 (<sup>35</sup>Cl and <sup>37</sup>Cl respectively) corresponding to C<sub>10</sub>H<sub>15</sub>Cl<sup>+</sup> and an intense peak at 135 (C<sub>10</sub>H<sub>15</sub><sup>+</sup>), whereas 1,3-dichloroadamantane gave weak signals at *m/e* 204, 206, and 208 corresponding to C<sub>10</sub>H<sub>14</sub>Cl<sub>2</sub><sup>+</sup>. Intense peaks were observed at 169 and 171 corresponding to C<sub>10</sub>H<sub>14</sub>Cl<sup>+</sup> and at 133 (C<sub>10</sub>H<sub>13</sub><sup>+</sup>).

**Oxidation in Acetic [<sup>2</sup>H]Acid.**—A solution of cobalt(III) acetate was prepared in pure DOAc as solvent by dissolving dry cobalt(III) acetate in 99% DOAc. Dry cobalt(III) acetate has been prepared by lyophilisation of the acetic acid solution of cobalt(III) acetate followed by addition of DOAc and repeating the lyophilisation. The lyophilisation-dissolution process was twice repeated until <2% acetic

acid could be detected by n.m.r. spectroscopy in the recovered DOAc. The oxidation experiments were performed as usual and the deuterium content in the starting material was evaluated by high resolution mass spectroscopy. No incorporation (<1%) was detected after oxidation of pentane whereas some isotope exchange (6%) was observed with cyclohexane but this was not significant as the isotope-exchange reaction took place to the same extent in a blank experiment in the absence of any cobalt(III) acetate.

We are indebted to Drs. J. Hanotier and P. de Radzitzky for helpful discussions.

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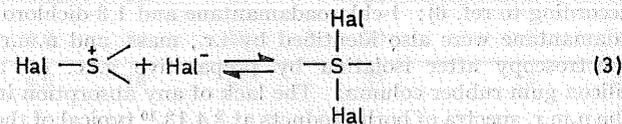
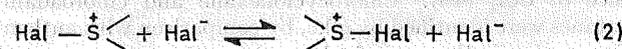
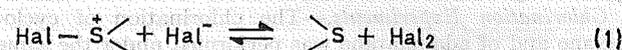
### Racemization of Sulphoxides with Halide Ions anchimerically assisted by a Carboxy-group. The Different Behaviour of Chloride and Bromide Ions

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The kinetics of the racemization of (–)-2-isopropylsulphinylbenzoic acid (Ib) catalysed by Cl<sup>–</sup> and Br<sup>–</sup> have been studied in aqueous perchloric acid, and compared with those of the (–)-methyl analogue (Ia). In racemization with Cl<sup>–</sup> the steric effect (*k*<sub>(Ia)</sub>/*k*<sub>(Ib)</sub> ca. 50) is similar to those found in the reactions at sulphur centres, whereas steric retardation is minimized in racemization with Br<sup>–</sup> (*k*<sub>(Ia)</sub>/*k*<sub>(Ib)</sub> ca. 6). Moreover the reactivity ratios, *k*<sub>Br</sub>/*k*<sub>Cl</sub> [3.100 and 500 for (Ib) and (Ia), respectively] are much higher than those found in the racemizations of normal sulphoxides (*k*<sub>Br</sub>/*k*<sub>Cl</sub> ca. 3). These results seem to indicate that attack by halide ions in the halogenosulphonium intermediate occurs at sulphur or at halogen depending on the nature of Hal<sup>–</sup>.

In recent years the reduction and racemization of sulphoxides catalysed by halide ions (I<sup>–</sup>, Cl<sup>–</sup>, Br<sup>–</sup>) in aqueous acidic media have been studied in detail,<sup>1–8</sup> however the loss of optical activity of the sulphinyl group is still an open question.

The following schemes have been proposed<sup>1–4</sup> to explain racemization (Hal = Br or Cl): (i) formation of sulphide and halogen [equation (1)], with equilibrium (1) largely shifted to the left; (ii) fast halogen exchange of the halogenosulphonium ion [equation (2)]; (iii) formation of an achiral dihalogenosulphurane intermediate [equation (3)].



† This is not the case in the reduction of (Ia) by I<sup>–</sup>, where attack by the second halide ion occurs in a relatively fast step.<sup>10</sup>

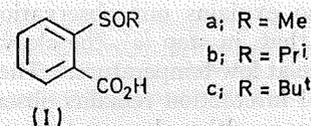
<sup>1</sup> D. Landini, F. Montanari, G. Modena, and G. Scorrano, *J. Amer. Chem. Soc.*, 1970, **92**, 7168.

<sup>2</sup> D. Landini, G. Modena, U. Quintily, and G. Scorrano, *J. Chem. Soc. (B)*, 1971, 2041.

<sup>3</sup> G. Scorrano, *Accounts Chem. Res.*, 1973, **6**, 132.

Since processes (1)–(3) occur after the rate-determining formation of halogenosulphonium ion for the sulphoxide examined,<sup>1</sup> no kinetic evidence can be found for any of them.

It has been shown<sup>9,10</sup> that in the 2-alkylsulphinylbenzoic acids (I) the reduction and racemization of



sulphinyl group are anchimerically assisted by the carboxy-group.

We have found<sup>10</sup> that in the racemization of (–)-(Ia) with chloride and bromide ions in aqueous perchloric acid the intervention of a second halide ion, leading to the loss of optical activity, is rate determining.† Therefore with compounds such as (I) it is, in principle, possible to differentiate process (1) from processes (2)

<sup>4</sup> K. Mislow, T. Simmons, J. T. Melillo, and A. L. Ternay, *J. Amer. Chem. Soc.*, 1964, **86**, 1452.

<sup>5</sup> R. A. Streker and K. K. Andersen, *J. Org. Chem.*, 1968, **33**, 2234.

<sup>6</sup> J. H. Krueger, *Inorg. Chem.*, 1966, **5**, 132.

<sup>7</sup> I. Ookuni and A. Fry, *J. Org. Chem.*, 1971, **36**, 4097.

<sup>8</sup> R. Curci, F. Di Furia, A. Levi, and G. Scorrano, *J.C.S. Perkin II*, 1975, 408.

<sup>9</sup> S. Allenmark and C. E. Hackberg, *Acta Chem. Scand.*, 1968, **22**, 1964.

<sup>10</sup> D. Landini, F. Rolla, and G. Torre, *Internat. J. Sulfur Chem. (A)*, 1972, **2**, 43.

and (3) by studying the influence of steric factors on the rate of racemization. Indeed pathways (2) and (3), involving attack of the second halide ion at the sulphur atom, must be subject to steric retardation, whereas the latter should be minimized in the case of (1), where attack occurs at halogen.

TABLE 1

p*K*<sub>a</sub> Value of sulphoxide (Ib) in HClO<sub>4</sub> from u.v. data at 25°

Acidity function	p <i>K</i> <sub>a</sub> <sup>a</sup>	Slope <sup>b</sup> (ν)
H <sub>0</sub> + log [H <sup>+</sup> ]	–1.85	0.56 (9 986)
H <sub>A</sub>	–2.25	0.98 (9 976)

<sup>a</sup> The reliability of the data is to be considered within ±0.2.<sup>11</sup> Slopes are evaluated by least squares analysis from plots of log ([SOH<sup>+</sup>]/[SO]) + H<sub>0</sub> versus H<sub>0</sub> + log [H<sup>+</sup>] and of log ([SOH<sup>+</sup>]/[SO]) versus –H<sub>A</sub>, respectively.

### RESULTS

The rates of chloride and bromide ion racemization of (–)-2-methylsulphinylbenzoic acid (Ia)<sup>10</sup> in aqueous perchloric acid have been compared to those of the (–)-isopropyl analogue (Ib). Unfortunately it was not possible to examine the behaviour of the *t*-butyl derivative (Ic),

(2.1–7.2M-HClO<sub>4</sub>) the sulphoxides are substantially protonated,<sup>11</sup> the reaction rate should be expressed in equation

$$\text{rate} = k_{\text{obs}}[\text{SO}]_{\text{st}} \quad (4)$$

(5).<sup>\*</sup> The amount of protonated sulphoxide (Ib) was

$$\text{rate} = k'[\text{SOH}^+] \quad (5)$$

evaluated from its thermodynamic p*K*<sub>a</sub> value and the acidity function H<sub>A</sub>.<sup>1</sup> The protonation equilibrium of (Ib) in perchloric acid was measured by a u.v. spectroscopic technique,<sup>11</sup> and thermodynamic p*K*<sub>a</sub> value, evaluated by the Bunnett and Olsen equation<sup>12</sup> and on the H<sub>A</sub> scale, is –1.85 and –2.25, respectively.† The data are collected in Table 1.

Since a plot of log ([SOH<sup>+</sup>]/[SO]) against –H<sub>A</sub> is linear with a slope of ca. 1 (Table 1), the H<sub>A</sub> acidity function can be used, as a good approximation, to describe the acid-base behaviour of sulphoxide (Ib). Thus the rate constant *k*', which takes into account protonation of sulphoxide (Ib) was evaluated, as previously reported,<sup>1</sup> from equation (6).

$$k' = k_{\text{obs}}(h_{\text{A}} + K_{\text{a}})/h_{\text{A}} \quad (6)$$

Table 2 shows that the rate coefficient *k*' still depends on

TABLE 2

Rate constants for racemization of (Ib) with halide ions in aqueous perchloric acid at 25°

Hal <sup>–</sup>	[H <sup>+</sup> ]/M	–H <sub>0</sub> <sup>a</sup>	–H <sub>A</sub> <sup>a</sup>	10 <sup>5</sup> <i>k</i> <sub>obs</sub> /s <sup>–1</sup>	5 + log <i>k</i> '/s <sup>–1</sup>	α <sup>c</sup> (ν)
Cl <sup>–</sup> <sup>d</sup>	4.10	1.91	1.72	1.64	0.856	1.26 (0.995 3)
	5.19	2.50	2.08	10.4	1.411	
	5.96	2.92	2.35	81.3	2.163	
	6.60	3.32	2.60	244	2.547	
	7.17	3.70	2.84	939	3.072	
	2.09	0.94	0.91	4.39	2.002	1.38 (0.996 1)
Br <sup>–</sup> <sup>d</sup>	2.59	1.16	1.15	14.0	2.276	
	2.98	1.35	1.31	31.4	2.484	
	3.37	1.54	1.45	99.1	2.860	
	4.10	1.87	1.69	397	3.264	

<sup>a</sup> Corrected for salt effect.<sup>1</sup> <sup>b</sup> The p*K*<sub>a</sub> value used is –2.25. <sup>c</sup> Slopes (α) were evaluated by least squares analysis from plots of log *k*' versus –H<sub>0</sub>. <sup>d</sup> From sodium chloride (0.4M) and bromide (0.2M).

TABLE 3

Dependence of rate constants for racemization of (Ib) on [Hal<sup>–</sup>] in aqueous perchloric acid at 25°

Hal <sup>–</sup>	[Hal <sup>–</sup> ]/M	[H <sup>+</sup> ]/M	–H <sub>0</sub> <sup>a</sup>	10 <sup>5</sup> <i>k</i> <sub>obs</sub> /s <sup>–1</sup>	5 + log <i>k</i> '/s <sup>–1</sup>	–(log <i>k</i> ' + αH <sub>0</sub> ) <sup>b</sup>	s <sup>c</sup> (ν)
Cl <sup>–</sup>	0.2	5.19	2.46	2.08	0.729	7.372	2.07 (0.9993)
	0.3	5.19	2.48	4.94	1.097	7.027	
	0.4	5.19	2.50	10.4	1.411	7.637	
	0.5	5.19	2.52	16.9	1.612	6.558	
Br <sup>–</sup>	0.1	2.59	1.14	2.52	1.544	5.033	2.24 (0.9997)
	0.2	2.59	1.16	14.0	2.274	4.327	
	0.3	2.59	1.18	35.6	2.666	3.959	
	0.4	2.59	1.20	72.8	2.963	3.686	

<sup>a</sup> Corrected for salt effect.<sup>1</sup> <sup>b</sup> α = 1.26 and 1.38 for reactions with chloride and bromide ions, respectively (see Table 2). <sup>c</sup> Slopes (s) were evaluated by least squares analysis from plots of –(log *k*' + αH<sub>0</sub>) versus log [Hal<sup>–</sup>].

since it undergoes an acid-catalysed decomposition faster than the reaction with halide ions.<sup>3</sup>

The reactions of (Ib), carried out at 25° with a large excess of halide ion and acid, follow the first-order kinetic equation (4) up to ≥80% conversion. The experimental rate constant, *k*<sub>obs</sub>, strongly depends on the acidity of medium. Since in the range of acid concentration used

\* [SOH<sup>+</sup>] and [SO] represent the concentration of protonated and free sulphoxide, respectively, and [SO]<sub>st</sub> stands for the stoichiometric concentration of sulphoxide.

† Similar differences have been found for other sulphoxides. For a discussion of the comparison between the two series of values, see refs. 1 and 11.

the acidity of the medium. Experimentally we found that log *k*' against H<sub>0</sub> is linear with slope (α) ca. 1, showing that a second proton intervenes before or during the rate-determining step (Table 2). The reaction order in halide ions was evaluated by plotting log *k*' + αH<sub>0</sub> versus log [Hal<sup>–</sup>], taking into account the salt effect on the H<sub>0</sub> acidity function and the complex dependence of the rate constant on the acidity of the medium, as previously described.<sup>1,10</sup>

<sup>11</sup> D. Landini, G. Modena, G. Scorrano, and F. Taddei, *J. Amer. Chem. Soc.*, 1969, **91**, 6703.

<sup>12</sup> J. Bunnett and F. P. Olsen, *Canad. J. Chem.*, 1966, **44**, 1899.