PERKIN 2

Determination and interpretation of second order rate constants for the addition of hydrogen halides to alkenes

Robert Borgeaud, Henry Newman, Arabella Schelpe, Veronica Vasco and D. E. Peter Hughes *

Westminster School, 17 Dean's Yard, London, UK SW1P 3PB

Received (in Cambridge, UK) 10th September 2001, Accepted 13th December 2001
First published as an Advance Article on the web 11th March 2002

An extensive range of second order rate constants for the addition of hydrogen halides to alkenes in 98% v/v ethanoic acid (acetic acid)–water have been obtained by conductivity measurements. The rate constants are in the expected order of HF < HCl < HBr < HI. The rates with different alkenes cannot be rationalised solely by a consideration of carbocation stability and it has been necessary to consider steric effects in order to explain the observed order.

Introduction

Most of the previous work on the addition of hydrogen halides to alkenes has been done with HCl and HBr. The emphasis has been on the mechanism[1–8] of the reaction under different conditions and on the composition[9] and stereochemistry of the product.[10] Comparatively few data are available on the rate constants for the reaction,[6] and there are almost no data for the addition of HF and HI[11] to alkenes. It is, therefore, difficult to compare quantitatively the effect of changing the alkene and/or the hydrogen halide.

A convenient way to follow the reaction is by conductivity measurements. In pure ethanoic acid (acetic acid), the conductivity of hydrogen halides is too small to be followed conveniently. It is much larger, even in the presence of hydrocarbon, using 98% v/v ethanoic acid–water as a solvent. Under these conditions, conductivity is proportional to the concentration of the hydrogen halide.

In this paper, we show that the addition of hydrogen halides to a variety of alkenes shows overall second order kinetics. This suggests that the reaction takes place by an Ad_E2 type of mechanism with the addition of a proton to the alkene being the rate determining step. The presence of water in the solvent ionises the acids extensively and this raises doubts about the nature of the electrophilic attacking species.

Results and discussion

Variation of acid

In the absence of any hydrogen halide, the solvent displays a small conductivity, presumably due to ionisation of the water and/or ethanoic acid. Initially, the addition of a small amount of hydrogen halide gives a non-linear increase in conductivity (for example, HBr Fig. 1) but, at higher concentrations, the relationship is linear. In the experiments carried out, the concentration of the hydrogen halide used was restricted to the linear portion of the graph. Under these conditions, conductivity is proportional to the concentration when allowance has been made for the initial conductivity, κ (see Fig. 1). We also established that substitution of halide for alkene had no significant effect on the conductivity.

During the course of the reaction, the conductivities were measured using a computer. An exponential curve fitting program was used to evaluate both the first order rate constant, k_1, and the intercept of the conductivity axis, κ.

One system, HBr and 2-methylbut-1-ene, was studied in detail. With the alkene in excess, all the runs showed good first order behaviour up to the point when 90% of the HBr had been used up. When the initial alkene concentration was varied by a factor of five, and assuming that the reaction is first order with respect to alkene, k_2, the second order rate constant, was found to be constant to within 5%, the estimated accuracy of the experiment (Table 1).

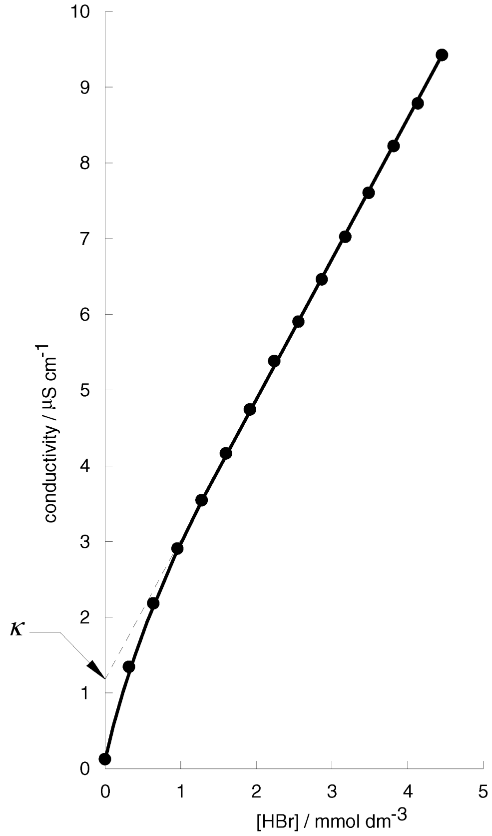


Fig. 1 Graph of conductivity against [HBr].

There was no significant difference in the rate constant when the electrodes were platinised, showing that catalysis at the electrode surface was not important. A change from the glass to the PTFE cell also showed no marked effect. One reaction was carried out in which measurements were taken until 98% of the HBr had been used up. At this point, there was a non-linear relationship between conductivity and HBr concentration and a calibration graph was used to convert conductivities to concentrations. A $\log_e$[HBr] against time graph was then drawn. This

DOI: 10.1039/b108199n

Table 1 Results of experiments with HBr and 2-methylbut-1-ene at 25.0 °C. The values of k_1 are the first order rate constants obtained when the alkene was in large excess. The second order rate constants, k_2, are obtained by dividing k_1 by the alkene concentration

Initial [HBr]/mmol dm^{-3}	Initial [alkene]/mol dm^{-3}	$k_1/10^{-2}$ s^{-1}	$k_2/10^{-2}$ dm^3 mol^{-1} s^{-1}
3.3[a]	0.368	1.00	2.72
3.3	0.368	1.00	2.72
4.0	0.368	1.02	2.76
4.0	0.368	1.02	2.76
4.4	0.368	1.00	2.72
4.4	0.368	1.06	2.87
4.4	0.184	0.504	2.74
4.4[a]	0.082	0.273	2.97
2.0	0.0736	0.205	2.61
2.0[a,b]	0.0736	0.214	2.73
2.0[a,c]	0.184	0.533	2.90
2.0[a,c]	0.0736	0.214	2.73
		Mean	2.77 (±0.03)

[a] 90% of HBr reacted. [b] With platinised electrodes. [c] PTFE cell.

Table 2 Second order rate constants, k_2/dm^3 mol^{-1} s^{-1} at 25.0 °C. Those marked * showed considerable reaction with the solvent and the measured values are, therefore, too small

Alkene	HF	HCl	HBr	HI
2-Methylbut-1-ene	*$3.3(\pm0.2) \times 10^{-3}$	$1.0(\pm0.03) \times 10^{-2}$	$2.77(\pm0.03) \times 10^{-2}$	$5.6(\pm0.6) \times 10^{-2}$
Number of experiments	2	3	12	5
2-Methylbut-2-ene	*$1.4(\pm0.8) \times 10^{-4}$	$2.4(\pm0.1) \times 10^{-3}$	$7.9(\pm0.3) \times 10^{-3}$	$2.7(\pm0.5) \times 10^{-2}$
Number of experiments	2	4	5	4
1-Methylcyclohexene	*$6.8(\pm1.1) \times 10^{-5}$	$9.5(\pm1.7) \times 10^{-4}$	$2.7(\pm0.7) \times 10^{-3}$	$5.4(\pm0.7) \times 10^{-3}$
Number of experiments	2	3	3	3
2,3-Dimethylbut-2-ene		*$5.6(\pm0.1) \times 10^{-4}$	$2.0(\pm0.2) \times 10^{-3}$	$2.1(\pm0.1) \times 10^{-3}$
Number of experiments		4	3	3
3,3-Dimethylbut-1-ene		*$2.7(\pm0.4) \times 10^{-4}$	$6.4(\pm1.3) \times 10^{-4}$	$1.4(\pm0.3) \times 10^{-3}$
Number of experiments		4	3	3
Hex-1-ene		*$1.9(\pm0.6) \times 10^{-4}$	$4.4(\pm1.5) \times 10^{-4}$	$8.2(\pm1.2) \times 10^{-4}$
Number of experiments		3	3	3
Phenylethene		*$3.4(\pm1.8) \times 10^{-5}$	*$6.3(\pm0.3) \times 10^{-5}$	
Number of experiments		2	2	
Cyclohexene		*$9.5(\pm1.3) \times 10^{-6}$	*$5.9(\pm1.2) \times 10^{-5}$	
Number of experiments		4	3	
(*Z*)-Pent-2-ene			*$7.2(\pm1.4) \times 10^{-5}$	
Number of experiments			4	
(*E*)-Pent-2-ene			*$3.5(\pm1.5) \times 10^{-5}$	
Number of experiments			4	

was linear along its whole length, corresponding to 5 half-lives. The value of k_2 obtained, (3.0×10^{-2} dm^3 mol^{-1} s^{-1}), was not included in the results as it was less accurate than the others that did not rely on a calibration graph.

Another reaction was carried out in which the initial concentrations of HBr and alkene were made the same (0.040 mol dm^{-3}). After converting conductivities into concentrations, a 1/concentration against time graph was drawn. This was linear until 95% of the alkene had been used up, showing that the reaction was second order overall. The value of the rate constant obtained (1.8×10^{-2} dm^3 mol^{-1} s^{-1}) was somewhat lower than those shown in Table 1. The difference can be attributed to a change in ionic strength of the solution.

The products were analysed using gas chromatography. Apart from the peaks due to alkene and to ethanoic acid, only one other peak was observed. The retention time of this peak was identical to that of a sample of pure 2-bromo-2-methylbutane. The peak was not 2-methylbutan-2-ol, 2-methyl-2-butyl ethanoate or 1-bromo-2-methylbutane as samples of all these substances were shown to have different retention times. Thus, for the reaction of HBr with 2-methylbut-1-ene, no anti-Markownikoff addition was observed and there was no significant reaction with the solvent.

For the alkenes used, the reactions with HCl, HBr and HI all exhibited second order kinetics. The results are shown in Table 2. Some reactions showed significant deviation from an exponential curve after one half-life. This was due to the alkene reacting with water and/or ethanoic acid to form an alcohol and/or an ester. While substitution of halide for alkene had no effect on conductivity, substitution of alcohol or ester for alkene resulted in an increase in conductivity, presumably because of changes to the relative permittivity of the medium. The overall result of reaction with the solvent is that the value k_2 obtained from conductivity measurements is too low. The effect was most pronounced with HCl. Analysis of the product obtained by treating HCl with 2-methylbut-1-ene showed that 15% of the product was alcohol and ester but this figure rose to 50% when HCl reacted with 2,3-dimethylbut-2-ene. The latter reaction (but not the former) showed significant deviation from a simple exponential curve after one-half life. We decided to include such results in Table 2, to mark them with an asterisk and to note that the measured values were too low. Determination of the constant κ, using the exponential curve fitting program, enabled us to find if there had been significant reaction with the solvent, because the greater the amount of this reaction, the larger the value of κ.

As the oxidation of HI to iodine is catalysed by light, reactions with HI were carried out in a vessel made light-proof with a double thickness of black polyethene. Oxidation was also minimised by the addition of 1% of phosphinic acid to the reaction mixture. By this means, there was no obvious production of I_2 when the reaction was completed in a few hours. For reactions that were left overnight, some iodine was produced. These reactions have been omitted from Table 2 as the production of significant amounts of I_2 would have decreased [HI], making k_2 too large. It is also known that iodine acts as a

Table 3 Increase in conductivities of the acids for an increase in concentration of 1.00×10^{-3} mol dm^{-3}

Acid	Conductivity/μS cm^{-1}	Degree of ionisation
$HClO_4$	4.92	1.0 (assumed)
HI	2.26	0.46
HBr	1.95	0.40
HCl	1.20	0.22
HF	0.10	0.020

catalyst under anhydrous conditions.[3] We, however, found no significant difference in the rate of reaction when small quantities of iodine were added to the reaction mixture.

The results with HF were unusual. The three most reactive alkenes produced a drop in conductivity as the reaction progressed, and k_2 was evaluated from the conductivity change in the usual way. The other alkenes produced an increase in conductivity, presumably because the increase in conductivity caused by production of alcohol and ester was larger than the small decrease produced by reaction with the hydrogen halide. A similar result was found with HCl and the least reactive alkenes. We have omitted these results from Table 2. Analysis of the product obtained by reacting HF with 2-methylbut-1-ene showed the presence of 2-fluoro-2-methylbutane (25%), 2-methylbutan-2-ol (70%) and a small amount of 2-methyl-2-butyl ethanoate. The large alcohol/ester ratio differed from the much smaller ratio found with HCl. In the solvent used, HF was almost un-ionised and presumably tended to hydrogen bond with itself rather than to water molecules; there would have been, therefore, more free water molecules in the HF reaction mixture than in the HCl reaction mixture, which may be the reason for the different alcohol/ester ratios found.

In order to estimate the degree of ionisation of the acids, their conductivities were compared with that of $HClO_4$. All showed lower conductivities (Table 3). If we assume that the $HClO_4$ was completely ionised and that the molar conductivities of all the ionised acids were approximately the same (as they are in pure water), it is possible to estimate the degree of ionisation of each acid.

Since the ratios k_2(HI) : k_2(HBr) : k_2(HCl) are consistently larger than 0.46 : 0.40 : 0.22 suggested by the ionisation data, it seems unlikely that H_3O^+ is the principal electrophile. This was confirmed as follows.

(i) If H_3O^+ was acting as an electrophile, the addition of $HClO_4$ would increase the rate of the reaction. When $[H_3O^+]$ was increased by a factor of 7, by adding $HClO_4$ to the HBr–2-methylbut-1-ene reaction mixture, the rate of the reaction increased by only 1.5 times. This increase was not due to any change in ionic strength of the medium as the addition of an identical concentration of $KClO_4$, instead of $HClO_4$, slightly decreased rather than increased the reaction rate. The small increase in reaction rate might have been due to addition of H_3O^+ to the alkene as a minor reaction, but it can also be interpreted as being due to an increase in the concentration of undissociated HBr, resulting from suppression of the ionisation of the HBr by the addition of $HClO_4$. This latter suggestion is supported by conductivity measurements as the conductivity of HBr is reduced in the presence of $HClO_4$. No such reduction in conductivity was found on addition of an equal concentration of $KClO_4$.

(ii) The rate of the reaction of HBr with 2-methylbut-1-ene was determined in solvents whose polarity was decreased by increasing the proportion of hexane (Table 4). If the reaction was between H_3O^+ and alkene, a plot of $\log_e k_2$ against $1/\varepsilon$ should be a straight line[12] with slope $\frac{e^2}{8\pi\varepsilon_0 kT}\left(\frac{1}{r} - \frac{1}{r_\ddagger}\right)$ where r is the radius of the ion and $r_\ddagger$ is the distance over which the charge is distributed in the transition state. This must have a positive value as $r_\ddagger > r$. If r and $r_\ddagger$ are assumed to be 0.1 and 0.3 nm respectively, the slope should be approximately +200. The measured value was about −20. The negative sign and the small value exclude the possibility of reaction between an ion and a neutral molecule but are consistent with a reaction between two molecules.

Table 4 Variation of the rate constant of the reaction between HBr and 2-methylbut-1-ene with the relative permittivity of the medium. The relative permittivity was changed by varying the proportion of hexane in the solvent

Relative permittivity, ε	$k_2/10^2$ dm^3 mol^{-1} s^{-1}
5.48	1.10
6.56	1.49
7.23	2.61
7.46	2.77
7.65	2.97
7.66	3.22

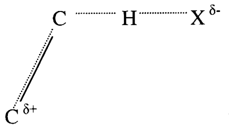
Variation of alkene

The most reactive alkenes form tertiary carbocations (the first four in Table 2). As 2,3-dimethylbut-2-ene contains two carbon atoms that can form tertiary carbocations, it might be expected to react the fastest, as it does with bromine in methanolic sodium bromide.[13] With HCl, HBr and HI it consistently reacted the slowest. Presumably the methyl groups on the carbon atom adjacent to the reaction centre either sterically hindered the incoming electrophile or their bulk destabilised the planar tertiary carbocation. The loss of one methyl group (2-methylbut-2-ene) resulted in an increase in rate of approximately 4 times, and the loss of two methyl groups (2-methylbut-1-ene) resulted in an increase in rate of approximately 20 times.

Steric effects would have been most important if the incoming electrophile was large and it may be that solvated HX, attached either to water or ethanoic acid, was the attacking species.

The following two transition states are likely for the reaction.

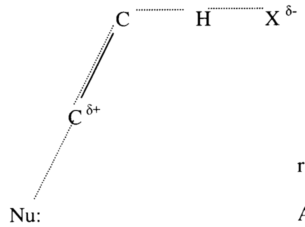
A



rate = k[alkene] [HX]

Ad_E2 mechanism

B



rate = k[alkene][HX][Nu:]

Ad_E3 mechanism

If the reactions with HF, HCl, HBr and HI had taken place by the second, Ad_E3, mechanism, a halide ion would have been involved in the transition state. As $[X^-]$ was proportional to [HX], any reaction by this mechanism should have shown overall third order, rather than second order, kinetics. This was not the case with HBr and 2-methylbut-1-ene. This conclusion was different to the results found by Fahey[14,15] for the addition of HCl and HBr in anhydrous ethanoic acid. Under these conditions, and in the presence of a high concentration of Cl^- ions, the second mechanism predominated. Our results showed that, in the presence of water, the mechanism appeared to be Ad_E2, even though the Cl^- ion concentration was fairly high. This suggested that water stabilised the carbocation so that its lifetime was long compared to the time taken for a Cl^- ion to diffuse to it. Under these conditions, the addition of the proton was the rate determining step and the Cl^- ion was not involved in the transition state. When the alkene reacted with the solvent to form an ester (or an alcohol), either, or both, mechanisms could have been operating.

To confirm that the Ad_E2 mechanism predominates, the reaction of HCl with 2,3-dimethylbut-2-ene was studied in the presence of added KCl. When the Cl^- ion concentration was increased by 15 times, the rate increased only 1.3 times, a result similar to that found when $HClO_4$ was added to the HBr–2-methylbut-1-ene reaction mixture. While the increase in rate is consistent with some participation by an Ad_E3 mechanism, it is equally likely that it is due to an increase in the concentration of undissociated HCl by suppression of ionisation.

Under anhydrous conditions, phenylethene partially polymerises unless the temperature is kept below −70 °C.[16] In the presence of water and in the presence of the inhibitor 4-*tert*-butylcatechol, polymerisation does not appear to be a problem. The rate constants for phenylethene are smaller than those for other terminal alkenes. This can be attributed to the reduction in the availability of the π electrons of the double bond as a result of conjugation with the benzene ring.

Cyclohexene and the *E* and *Z* conformers of pent-2-ene all react at comparable rates. Although they contain two carbon atoms that can form secondary carbocations, their rates are slower than those for alkenes with a terminal double bond, that can form only one secondary carbocation. Possibly steric effects operate similar to those already discussed with the alkenes that form tertiary carbocations.

Experimental

Materials

The ethanoic acid and the hydrohalic acids were of AnalaR quality obtained from Merck. The HF was 48–51% obtained from Sigma-Aldrich. The alkenes were obtained from Sigma-Aldrich and most had a quoted purity in excess of 99%. The water was freshly prepared by glass distillation.

The standards used in the gas chromatography analysis were mainly obtained from Sigma-Aldrich. As neither 2-fluoro-2-methylbutane nor 2-methyl-2-butyl ethanoate was obtainable, impure samples were prepared as follows. 2-Fluoro-2-methylbutane was made by mixing 2-methylbutan-2-ol with concentrated HF for a week. The gas chromatography trace of the product showed a new peak with a retention time between that of the 2-methylbut-1-ene (bp 31 °C) and 2-chloro-2-methylbutane (bp 86 °C). A sample of 2-methyl-2-butyl ethanoate (bp 124 °C) was made by reacting 2-methylbutan-2-ol with ethanoyl chloride and distilling the product. The fraction collected between 122 and 124 °C, when analysed by gas chromatography, showed a major peak with a slightly larger retention time than that for 2-methylbutan-2-ol (bp 102 °C).

Method

For experiments with HCl, HBr and HI, a dipping electrode assembly was attached to a 24/29 adapter fitted to a 150 mm glass test tube. The electrodes were of shiny platinum and the measured cell constant was 0.92(±0.03) cm^{-1}. The electrical input was supplied by a 5 V, 500 Hz audio oscillator. The voltage and current readings were fed to a computer, using a pico ADC-100 analogue to digital converter. The results were processed to find the parameters in an exponential curve fitting program, including the determination of the final reading, κ, for the run. When the curve showed deviation from exponential behaviour, the rate constant, k_1, was found from the initial portion of the curve. The reaction was started by shaking the alkene with the acid; subsequently no stirring was used.

The experiments with HF were conducted in a PTFE cell. This was made from a 10 cm^3 Teflon centrifuge tube, containing shiny platinum wires in PTFE tubing secured in a polypropene stopper. The measured cell constant was 0.61(±0.06) cm^{-1}. The composition of the reaction mixture was similar to that for the other acids, but with a total volume of 5.0 cm^3, rather than 25.0 cm^3. The results with this cell were less reliable than those obtained with HCl, HBr and HI.

All the experiments were carried out in a water bath, at a temperature of 25.0 ± 0.04 °C.

In the experiments, the alkene was in large excess. Typically the hydrogen halides were between 0.001 and 0.005 mol dm^{-3} and the alkene between 0.05 and 0.3 mol dm^{-3}. The total volume of the acids was 24.0 cm^3 and the hydrocarbon added 1.00 cm^3. If the volume of alkene added was less than 1.00 cm^3, the difference was made up with hexane which had a similar relative permittivity to the alkenes used. The relative permittivity, calculated value 7.64,[17] of the reaction mixture was, therefore, constant.

Analysis by gas chromatography

The products of the reaction between HBr and 2-methylbut-1-ene were analysed with a Unicam 610 series gas chromatogram, using a column temperature of 110 °C. The products of the reactions of HCl and HF with 2-methylbut-1-ene and HCl with 2,3-dimethylbut-2-ene were analysed with a Perkin Elmer Autosystem, using a column temperature of 130 °C. Both instruments used a flame ionisation detector and the temperatures of the detectors and injection ports were 200 °C. Both instruments had columns 7′ long, containing 10% Carbowax 1500 on Chromosorb WHP.

Acknowledgements

Our thanks to Dave G. Davies for technical help and for writing the conductivity program, and to Tom Barnet-Lamb for writing the curve-fitting program. Particular thanks are due to Dr Ed H. Smith of the Chemistry Department, Imperial College of Science, Technology and Medicine who spent much time giving advice and who also gave invaluable help with the analysis using gas chromatography. Our thanks also to Professor Michael Spiro of the same department who gave encouragement throughout the project.

References

1 G. H. Schmid and D. G. Garrat, in *The Chemistry of Double Bonded Functional Groups*, ed. S. Patel, John Wiley, Chichester, 1977, Supplement A, Part 2, p. 732.
2 G. A. Olah and A. Molnár, in *Hydrocarbon Chemistry*, John Wiley, New York, 1995, p. 205.
3 G. B. Sergeev, V. V. Smimov and T. N. Rostovshchikova, *Russ. Chem. Rev. (Engl. Transl.)*, 1983, **52**, 259.
4 T. H. Lowry and K. S. Richardson, in *Mechanism and Theory in Organic Chemistry*, Harper and Row, New York, 1981, p. 513.
5 D. J. Pasto, G. R. Meyerand and B. Lepeska, *J. Am. Chem. Soc.*, 1974, **96**, 1858.
6 R. C. Fahey and C. A. McPherson, *J. Am. Chem. Soc.*, 1969, **91**, 3865, 4199; R. C. Fahey and C. A. McPherson, *J. Am. Chem. Soc.*, 1971, **93**, 2445.
7 Y. Pocker, K. D. Stevens and J. J. Champoux, *J. Am. Chem. Soc.*, 1969, **91**, 4199.
8 T. Okuyama, K. Izawa and T. Fueno, *J. Am. Chem. Soc.*, 1973, **95**, 6749.
9 R. C. Fahey, in *Topics in Stereochemistry*, ed. E. L. Eliel and L. Alinger, Interscience Publishers, New York, 1968, Vol. 3, p. 237.
10 R. C. Larock and W. W. Leong, in *Comprehensive Organic Synthesis*, ed. B. M. Trost, Pergamon Press, New York, 1991, Vol. 4, p. 269.
11 H. Cohn, E. D. Hughes, M. H. Jones and M. G. Peeling, *Nature*, 1952, **169**, 291.
12 K. J. Laidler and H. Eyring, *Ann. N. Y. Acad. Sci.*, 1940, **39**, 303.
13 J. E. Dubois and G. Mouvier, *Bull. Soc. Chim. Fr.*, 1968, 1426.
14 R. C. Fahey, M. W. Monahan and C. A. McPherson, *J. Am. Chem. Soc.*, 1970, **92**, 2810.
15 R. C. Fahey, C. A. McPherson and R. A. Smith, *J. Am. Chem. Soc.*, 1974, **96**, 4535.
16 M. S. Kharasch and M. Kleinman, *J. Am. Chem. Soc.*, 1943, **65**, 11.
17 C. Wohlfarth, in *Handbook of Chemistry and Physics*, ed. D. R. Lide, 75th edition, Vol. 6, p. 155.