

Inner Sphere and Outer Sphere Electron Transfer to Methyl Iodide. Deuterium and ^{13}C Kinetic Isotope Effects

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Deuterium and ^{13}C kinetic isotope effects (KIEs) have been determined for the conversion of methyl iodide into methyl radical via inner sphere ET (electron transfer) and via outer sphere ET. The α -deuterium KIE was found to be very high for inner sphere ET and very low for outer sphere ET, while the ^{13}C KIE was high for inner sphere ET, but also significant for outer sphere ET.

The use of carbon KIEs for distinguishing between inner and outer sphere ET reactions to methyl iodide is therefore not appropriate, while α -D KIEs are well suited.

The reason for the high α -D KIEs in inner sphere ET is the 'stiffer' C–H bonds in methyl iodide as compared with the more pliable C–H bonds in methyl radical. Formation of methyl radical by ET from methyllithium and methylmagnesium halide has very low α -D KIEs since the organometal reagents, like methyl radical, have low force constants in their carbon–hydrogen bonds.

Kinetic isotope effects (KIEs) are useful in the study of organic reaction mechanisms¹ and have been used extensively in the study of nucleophilic substitutions.² Less common are attempts to assign radical-type reaction mechanisms on the basis of observed KIEs.^{3–8}

Methyl radical may be generated from methyl iodide either by the direct transfer of an electron by outer sphere ET to form the radical anion transition state, which expels iodide, eqn. (1),



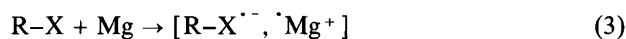
or indirectly by inner sphere ET, in which the electron is transferred together with an atomic fragment, eqn. (2).



In eqn. (1) there are no formal bond changes up to the transition state, while in eqn. (2) bonds both break and form in the transition state.

The mechanism of ET to alkyl halides has been under scrutiny in recent years. Ebersson and Shaik in a discussion based on orbital theory stated⁹ that outer sphere ET is an exception, which requires the absence of electronic interaction in the transition state. This condition is not fulfilled if the electron is donated from a radical anion, but ET from an inert electrode is considered outer sphere, since only weak coupling between substrate and metal orbitals is required in the transition state. It is reasonable to assume that this pertains also to ET from dissolving metals or, like here, from metals in solution.

KIEs may allow one to distinguish between the two types of ET.¹⁰ In the on-going discussion concerning the formation reaction of the Grignard reagent,^{6–8} an important contribution was given by Vogler *et al.*⁸ who used the absence of a ^{13}C KIE to conclude that the initial ET from magnesium to alkyl halide was outer sphere [eqn. (3)]



and not inner sphere [eqn. (4)].



To be able to make the conclusion the authors used the assumptions (1) that outer sphere ET is without ^{13}C KIE 'since the electron given up by the reducing agent is transferred to the oxidizing agent with no net bond breakage in either reaction partner,' and (2) that inner sphere ET has a significant KIE. Since both assumptions were deduced from theoretical considerations it seemed of importance to obtain experimental values for KIEs for typical ET reactions to an alkyl halide.

In the present work KIEs have been measured for ET to methyl iodide by both inner sphere and outer sphere ET.

Results and discussion

Inner sphere ET. Inner sphere ET to methyl iodide takes place in the reduction of methyl iodide with hydrogen

iodide at 250°C. The reaction has been studied in detail by several workers.¹¹⁻¹³ The mechanism has been found to consist of three steps [eqn. (5)–(9)] with an overall reaction (10).



The rate expression¹² according to this mechanism is given in eqn. (11).

$$\frac{d[I_2]}{dt} = \frac{d[CH_4]}{dt} = \frac{K_{5,6}^{1/2} [I_2]^{-1/2} k_9 [HI] K_{7,8} [CH_3I]}{1 + k_9 [HI]/k_8 [I_2]} \quad (11)$$

The rate constants and activation parameters for the reaction are known.^{12,13} Flowers and Benson found $k_9/k_8 \approx 0.13$ at 250°C.

The method adopted for determining KIEs was to let methyl iodide compete with methyl iodide-*d*₃ and to measure the amount of methanes formed in the initial phase of the reaction.

In a competition experiment the kinetic isotope effect at any moment is given in eqn. (12).

$$\frac{d[CH_4]}{d[CD_3H]} = \frac{K_{7,8}^H [CH_3I]}{K_{7,8}^D [CD_3I]} \times \frac{1 + k_9^D [HI]/k_8^D [I_2]}{1 + k_9^H [HI]/k_8^H [I_2]} \times \frac{k_9^H}{k_9^D} \quad (12)$$

For the initial reaction when $[HI] \gg [I_2]$ and concentrations of methyl iodides are almost unchanged the expression reduces to eqn. (13).

$$\frac{k_{1H}}{k_{1D}} = \frac{[CH_4]}{[CD_3H]} \times \frac{[CD_3I]_0}{[CH_3I]_0} \quad (13)$$

k_H/k_D represent the α -deuterium KIE for the inner sphere ET (7) and could be determined by means of GC by measuring the ratio of CH_4 to CD_3H after 2–8% conversion. The extent of the reactions was found by titration of the iodine produced.

In order to find the ¹³C KIE for reaction (7) a second competition experiment was performed between ¹³CH₃I and CD₃I. From the two ratios ¹²k/k_D and ¹³k/k_D the ¹³C isotope effect, ¹²k/¹³k, was found by division. The result was checked by an independent method by including ¹³CD₃I as the reference substance. The use of this compound in competition with either ¹²CH₃I or ¹³CH₃I allowed the determination of the ratios ¹²k/¹³k_D and ¹³k/¹³k_D, and as above, the calculation of ¹²k_H/¹³k_H by division. ¹²k_D/¹³k_D valid for trideuteriomethyl iodide was also obtained.

The results given in Table 1 show a large α -deuterium KIE ($k_H/k_D = 1.42$) for reaction (7) and a significant ¹³C KIE (¹²k/¹³k = 1.035). The values were determined at 523 K. At room temperature the values are expected to be higher although the temperature dependence of KIEs is complicated.¹⁵ A KIE of 1.42 at 250°C would according to the Arrhenius equation correspond to 1.84 at 20°C if zero-point energies were constant over the temperature range 20–250°C. ¹²k/¹³k = 1.035 at 250°C would change to 1.056 at 20°C on the same basis.

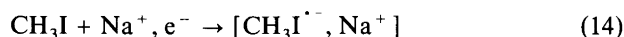
The reason for the large deuterium KIE when going from methyl iodide to methyl radical is the change of 'stiff' hydrogen-carbon bonds in the iodide to very 'pliable' C-H bonds in the radical.¹⁵ From the IR data available¹⁶ crude estimates would indicate a KIE, k_H/k_D , for reaction (2) of the order of 2.0 for the substitution of three α -hydrogens with deuterium. Methyl lithium and methylmagnesium halide, like methyl radical, have C-H bonds

Table 1. Observed KIEs for the reaction: MeI + HI → MeH + I₂. For the competition experiments with the 1:1 mixtures of the methyl iodides shown, the conversion in per cent and the KIE, k_H/k_D , measured as the ratio between the GC integrals of the methane-*d*₃ and the non-deuteriated methane are given.

¹² CH ₃ I/ ¹² CD ₃ I		¹³ CH ₃ I/ ¹² CD ₃ I		¹² CH ₃ I/ ¹³ CD ₃ I		¹³ CH ₃ I/ ¹³ CD ₃ I	
Conv.	KIE (%)	Conv.	KIE (%)	Conv.	KIE (%)	Conv.	KIE (%)
5.0	1.415	3.0	1.341	9.6	1.441	2.5	1.391
2.6	1.426	5.1	1.346	12.0	1.451	2.5	1.401
11.0	1.424	11.2	1.342	6.7	1.465		
7.5	1.420	2.0	1.353				
Average:							
1.421 ± 0.005		1.345 ± 0.006		1.452 ± 0.012		1.396 ± 0.007	
¹² k _H / ¹³ k _H = 1.035 ± 0.009				¹² k _D / ¹³ k _D = 1.041 ± 0.013			

with low force constants,¹⁷ and the formation of methyl radical by ET from methyl lithium (or methylmagnesium halide) to an acceptor will therefore have very low KIEs even for inner sphere ET.¹⁵

Outer sphere ET. The reaction of magnesium with alkyl halide investigated by Vogler *et al.* is heterogeneous, which may mean a complication of the reaction mechanism. A simple homogeneous outer sphere ET is the reduction of methyl iodide with a solution of sodium in ammonia, which through the rate-determining outer sphere ET (14), homolysis (15), hydrogen abstraction and radical recombination (16), leads to a mixture of methane and ethane.



For the sake of clarity eqns. (14) and (15) are given as separate steps though the intermediate is probably no more than a transition state.

By letting a large excess of a 1:1 mixture of methyl iodide and trideuteriomethyl iodide compete for a small amount of sodium, the deuterium KIE for the rate-determining ET may be determined by GC analysis of the reaction products. The five products: CH₄, CD₃H, C₂H₆, C₂D₆ and CH₃CD₃ give, using a suitable molecular sieve capillary column, five discrete GC peaks. Summation of the integrals originating from CH₃ and CD₃ respectively, made the determination of ¹²k_H/¹²k_D possible.

As before, competition between ¹³CH₃I and ¹²CD₃I gave ¹³k/¹²k_D, using an identical procedure. Since the observed KIEs were now smaller it was an advantage to use

¹³CD₃I in competition with ¹²CH₃I since the two effects were added to give an effect about 10 times the accuracy of the method. The ratio between the various observed KIEs gave ¹²k_H/¹³k_H and ¹²k_D/¹³k_D, which are identical to within experimental uncertainty.

The results are given in Table 2. It is seen that the KIEs in the outer sphere ET are small but significant, and that the α-deuterium effect for three deuteriums equals the effect of the ¹³C effect. Compared with the very large α-deuterium KIE for the inner sphere ET described above a value of 2.5% or about 0.8% per deuterium suggests that the carbon-hydrogen bonds are nearly unchanged in the transition state. This is in accordance with the Franck-Condon principle: ET is faster than rehybridisation and radical character of the methyl group is developed only after the transition state. The ¹³C isotope effect, however, amounts to 2.5% which is more than 50% of the effect expected if the carbon-iodine bond were totally broken. This indicates a considerable weakening of the carbon-iodine bond in the transition state in which an electron is placed in an antibonding orbital.

The ratio of ethanes to methanes was regularly close to 0.43 and the H/D ratio in the ethanes was of the order of 1.04. This indicates a higher reactivity of the CD₃ radical than of CH₃ toward the solvent ammonia, since the radicals that fail to abstract hydrogen will recombine to form ethanes. Apparently the radical, which is the slowest in the formation reaction, is the fastest to attack ammonia.

The results obtained are not in agreement with the conclusions made by Vogler *et al.* who found a ¹³C KIE < 0.08% for the reaction of magnesium with methyl iodide. There seems to be no reason to expect a lower ¹³C KIE for an outer sphere ET from magnesium to the halide than from Na⁺, e⁻, NH₃ to the same halide, even if the solvents are different. If a ¹³C KIE is really absent in the Grignard formation reaction, the reason may be that ET is not rate-determining. Since the reaction is heterogeneous diffusion to 'reactive spots' may be controlling. The problem will be approached in this laboratory.

Table 2. Observed KIEs for the reaction: MeI + e⁻ → Me[·] + I⁻ in liquid ammonia at -34 °C, determined as the ratio of products (see the text) after 7% conversion.

	¹² CH ₃ I- ¹² CD ₃ I k _H /k _D	¹³ CH ₃ I- ¹² CD ₃ I k _H /k _D	¹² CH ₃ I- ¹³ CD ₃ I k _H /k _D	¹³ CH ₃ I- ¹³ CD ₃ I k _H /k _D
	1.027	0.998	1.046	1.031
	1.016	0.992	1.059	1.035
	1.036	0.993		
	1.024	1.003		
	1.022	1.003		
	1.019			
	1.021			
	1.025			
Average:	1.024 ± 0.006	0.998 ± 0.005	1.053 ± 0.009	1.033 ± 0.006
	¹² k _H / ¹³ k _H = 1.026 and 1.019 Average 1.023 ± 0.009		¹² k _D / ¹³ k _D = 1.028 and 1.035 Average 1.031 ± 0.009	

Experimental

Materials. Isotopically labelled compounds were purchased from Cambridge Isotope Laboratories. Isotopic purity >99%.

Methyl iodide–hydrogen iodide. A stock solution was prepared from 400.0 μl of methyl iodide and 400.0 μl of trideuteriomethyl iodide. A 22 ml ampoule with a 2 mm neck was equipped with a polyethylene filling tube. The ampoule was evacuated and sealed by keeping the tube in a sharply bent position by means of copper wire and plugging the opening with a glass stopper. By means of a Hamilton micro syringe 20 μl (ca. 50 mg) of the H/D methyl iodide mixture were added through the tube without adding air. 18 ml of dry hydrogen iodide were added and the ampoule was sealed and placed in an oven at 250°C for the time specified in Table 1. After cooling, a syringe containing 3 ml of water was connected to the ampoule before breaking the tip. The water absorbed the iodine and the remaining HI creating a partial vacuum, which was eliminated by admission of air. A sample of the head space was analysed by GC giving the relative concentrations of D/H methanes: $[\text{CH}_4]/[\text{CD}_3\text{H}]$. Three deuteriums in methane enable complete separation of the GC peaks on the 75 m capillary column, while substitution of ^{12}C with ^{13}C does not change the retention time. The amount of iodine produced was found by titration with sodium thiosulfate. The deuterium isotope effect was calculated from eqn. (13). Identical procedures were used using mixtures of $^{13}\text{CH}_3\text{I}$ – $^{12}\text{CD}_3\text{I}$, $^{12}\text{CH}_3\text{I}$ – $^{13}\text{CD}_3\text{I}$, and $^{13}\text{CH}_3\text{I}$ – $^{13}\text{CD}_3\text{I}$. The ratios between $[\text{CH}_3\text{I}]_0$ and $[\text{CD}_3\text{I}]_0$ were found by measuring the ratios of methanes by GC after reducing 1 μl of the methyl iodide mixtures with 18 ml of gaseous HI in an ampoule at 350°C for 1.5 h.

The hydrogen iodide was produced by addition of 57% hydriodic acid to the bottom of a column filled with phosphorus pentoxide. After passage through the column the dry, colourless gas was collected in a 50 ml syringe and used immediately.

Methyl iodide–sodium in ammonia. In an argon-filled 10 ml ampoule was placed a 0.5 mg (0.022 mmol) pellet of sodium produced by means of a miniature 'cork drill' consisting of a sharpened stainless steel capillary 1 mm in diameter with a stainless steel plunger. The ampoule was evacuated and cooled in dry-ice/acetone. 3 ml of dry ammonia were admitted. The sodium dissolved producing a dark blue liquid. The ampoule was heated to -33°C and 20 μl of a 1:1 v/v mixture of methyl iodides (0.32 mM) were added, see above. The blue colour disappeared within 1 s. The ampoule was again cooled to -75°C and 5 ml of water were added with shaking. 2 ml of the gas phase were removed with a syringe and washed with 3 ml

of water after which 20 μl of the remaining gas were injected into the gas chromatograph. Ethane, ethane- d_3 and ethane- d_6 were separated on the GC column. In order to find the exact ratio of methyl iodides in the 1:1 starting mixtures, the same procedure was followed except for using a large excess of sodium (3 mg to 1 μl of methyl iodides). Using the calibration factors the KIEs were found according to eqn. (13).

Gas chromatography. A Hewlett–Packard 5890, Series II instrument equipped with a standard injector and FI detector was used. The column was a 75 m \times 0.32 mm 5 Å molecular sieve capillary column (Chrompack) with a layer thickness of 30 μm . The carrier gas was hydrogen, injection split 50:1. Retention times for methane and trideuteriomethane at 30°C were 21.57 min and 21.99 min, respectively. Elution of the ethanes followed after heating of the column to 150°C, after a total retention time of 50.04, 50.48 and 50.93 min for ethane- d_6 , ethane- d_3 and ethane, respectively. An HP integrator 3394 A was used.

The reproducibility of the area ratios was 0.2–0.3%. The determination of a KIE required two area ratios and was reproducible to within 0.5%. The measurements were repeated 2–7 times. The standard deviation found for the seven determinations of $^{12}k/k_D$ was, because of the identity of the procedure for all experiments, adopted as universal.

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