531. *Action of Alkali Metals on Organic Sulphur Compounds. Part I. The Cleavage of Thioanisole by Potassium in Ethereal and Hydrocarbon Solvents.*

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Potassium reacts with thioanisole in ethereal and hydrocarbon solvents with the primary formation of methyl and thiophenoxide anions. In benzene, and to a smaller extent in the other solvents studied, a small amount of the thioanisole seems to be cleaved with the primary formation of thiophenoxide anions and methyl radicals. The reaction in toluene affords a convenient preparation of benzylpotassium.

In a more general study of the donor and acceptor properties of bivalent sulphur, we have investigated the reaction between metallic potassium and various organic sulphides in solvents other than liquid ammonia or organic amines in the hope that an initially formed anion might be more stable therein. At room temperature in both ethereal and hydrocarbon solvents, however, although the reaction usually proceeds with the appearance of a colour which is rapidly discharged by oxygen, we have been unable, except in the case of dibenzothiophen, to detect any primary anion-radicals by electron spin resonance spectroscopy. Diamagnetic dianions would not, of course, be detected in this way.

In these solvents the reductive cleavage of organic sulphides proceeds smoothly and cleanly, usually with the formation of a thiol and a hydrocarbon. In particular, the cleavage of thioanisole proved to be a particularly simple system to study and we here report our observations on the stoicheiometry of this reaction in a variety of solvents in the hope that they throw some light on the general problem of the alkali-metal cleavage of thioethers.

From previous work,[1] it appears that, in general, thioethers are more readily attacked than ethers by alkali metals dissolved in liquid ammonia or amines. Thioanisole and sodium in liquid ammonia gave thiophenol in 73% yield,[2] and anisole is quantitatively cleaved to thiophenol and methane by potassium in liquid ammonia [3] but in low yield by sodium.[4] Table 1 shows our qualitative observations on the cleavage of thioanisole by potassium in four solvents. The yields of methane and thiophenol are in all cases approximately quantitative and no products other than these shown have been detected.

Table 1.

Reaction of potassium and thioanisole in various solvents.

	Products	
Solvent	Gaseous	In solution
$(MeO{\cdot}CH_2)_2$	CH_4, C_2H_6 (trace), C_2H_4 (trace)	PhSH, $MeO{\cdot}CH{:}CH_2$,* MeOH,† KOH †
Et_2O	CH_4, C_2H_4	
C_6H_6	CH_4, C_2H_6 (trace)	PhSH, KOH,† BzOH ‡
Toluene	CH_4	PhSH, KOH,† $CH_2Ph{\cdot}CO_2H$ ‡

* Identified as $MeO{\cdot}CHBr{\cdot}CH_2Br$ after bromination. † After hydrolysis; allowance was made for unused potassium. ‡ Extracted after carboxylation of the reaction mixture with CO_2.

For the reaction in 1,2-dimethoxyethane and in benzene we determined the amount of potassium that reacted and the amounts of methane, thiophenol, and hydroxide formed. The measurements were made with different concentrations of thioanisole and different amounts of potassium. The volume of the reaction mixture was kept constant as was the final volume of the hydrolysed mixture used for the determination of thiophenol and hydroxide. These results are shown graphically in the Figure, and the stoicheiometry of

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[1] (*a*) Truce, Tate, and Burdge, *J. Amer. Chem. Soc.*, 1960, **82**, 2872; (*b*) Truce and Breiter, *ibid.*, 1962, **84**, 1621, and references therein.

[2] Hughes and Thompson, *J. Proc. Roy. Soc. New South Wales*, 1948, **82**, 262.

[3] Freudenberg, Lantsch, and Piazolo, *Ber.*, 1941, **74**, 1886.

[4] Birch, *J.*, 1946, 593.

TABLE 2.

Stoicheiometry of the cleavage of thioanisole by potassium in dimethoxyethane and benzene.

Solvent	CH_4 : K	PhSH : K	OH^- : K	CH_4 : PhSH
$(MeO{\cdot}CH_2)_2$	0·525 ± 0·011	0·515 ± 0·020	0·477 ± 0·057	0·996 ± 0·035
C_6H_6	0·483 ± 0·013	0·522 ± 0·062	0·409 ± 0·054	0·913 ± 0·091

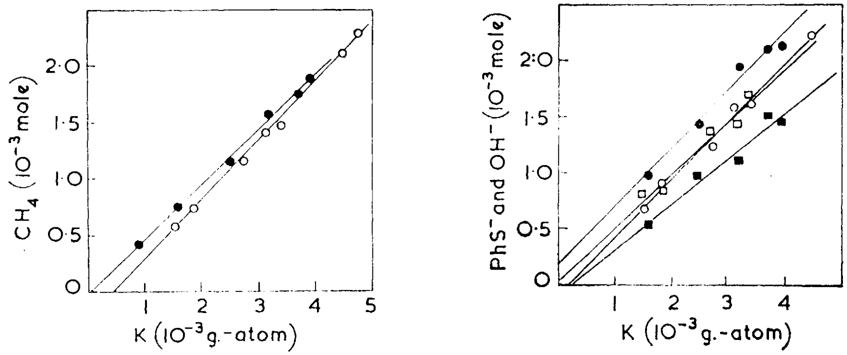
the reaction was determined from the slopes of these plots obtained by a least-squares analysis. These values are summarised in Table 2 with the probable errors at the 5% level. In this way, the effect of constant systematic errors (*e.g.*, the solubilities of methane and hydrogen in the solvent, the conversion of dissolved carbon dioxide into carbonate which is indistinguishable potentiometrically from thiophenoxide, etc.) is avoided. It is these errors which cause the straight lines of the Figure to be displaced from the origin.

It is generally accepted that the primary step in the reaction is the transfer of one or two electrons to the sulphide.[1b,5] Our results indicate that the reaction in dimethoxyethane is best described as a two-electron cleavage:

$$2K + PhSMe \longrightarrow PhS^- + Me^-$$

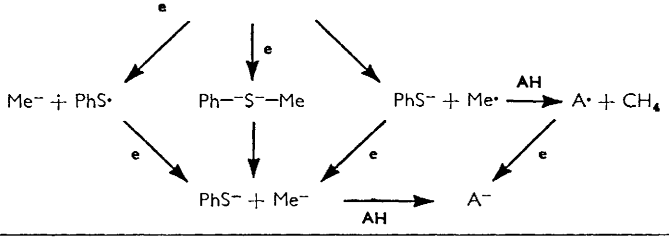
$$Me^- + (MeO{\cdot}CH_2)_2 \longrightarrow CH_4 + MeO^- + CH_2{:}CH{\cdot}OMe$$

By stoicheiometric methods alone it is impossible to determine the exact path taken to produce this overall reaction. Thus, if electron transfer from the metal to the radicals were faster than their rate of diffusion, no distinction could be made between the routes summarised in the chart. However, if any of the possible radicals became free from the surface it would be unlikely to react exclusively with the metal and more complex stoicheiometry would result.



(a) (b)

Quantitative determination of the products of the cleavage of thioanisole by potassium in solution in dimethoxyethane and benzene: (a) CH_4; (b) thiophenoxide (circles) and hydroxide (squares). Open symbols refer to dimethoxyethane, and full symbols to benzene, solutions.



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[5] Birch, *Quart. Rev.*, 1950, **4**, 69; Krug and Tocker, *J. Org. Chem.*, 1955, **20**, 1; Van Schooten, Knoterus, Boer, and Duinker, *Rec. Trav. chim.*, 1958, **77**, 935.

It was not possible to determine the methanol and methyl vinyl ether quantitatively, although their presence in approximately the expected concentration was demonstrated. In diethyl ether, however, methyl anions react to produce methane, ethylene, and ethoxide ions and the evolved gas was shown to be an equimolar mixture of methane and ethylene.

The significant departure of the ratio $CH_4 : K$ from the 0·5 required by an exclusively two-electron cleavage indicates that $5 \pm 2\%$ of the thioanisole is cleaved by a radical mechanism in which the free methyl radical reacts almost entirely by proton-abstraction from the solvent:

$$\mathrm{K + PhSMe \longrightarrow Ph{-}S^{-}{-}Me}$$
$$\mathrm{Ph{-}S^{-}{-}Me \longrightarrow PhS^{-} + Me\cdot}$$
$$\mathrm{Me\cdot + (MeO{\cdot}CH_2)_2 \longrightarrow CH_4 + MeO{\cdot}\dot{C}H{\cdot}CH_2{\cdot}OMe}$$
$$\mathrm{2Me\cdot \longrightarrow C_2H_6}$$

The observation of traces of ethane supports this conclusion. The expected values, if 5% of the reaction in dimethoxyethane proceeds by this mechanism, are given in Table **3**; they are in accord with experiment. The solvent radicals generated would probably lead to a variety of products, so making it difficult to isolate any one of them. In toluene, however, benzyl radicals are known to dimerise almost exclusively,[6] but we were unable to detect bibenzyl and estimate that not more than 3% of the thioanisole can have reacted by radical cleavage. This reaction, incidentally, provides a very convenient preparation of benzylpotassium as it appears to be quantitatively described by the equation, $2K + PhSMe + PhMe \longrightarrow PhSK + Ph{\cdot}CH_2K + CH_4$. The benzylpotassium may be separated from the thiophenoxide by dissolution in dimethoxyethane.

TABLE 3.

Theoretical stoicheiometry of cleavage of thioanisole with 5% (in dimethoxyethane) and 10% of radical cleavage (in benzene).

Solvent	$CH_4 : K$	$PhS^- : K$	$OH^- : K$	$CH_4 : PhS^-$
$(MeO{\cdot}CH_2)_2$	0·525	0·525	0·475	1·000
C_6H_6	0·475	0·550	0·450	0·865

In benzene the precision of our measurements was less than in dimethoxyethane and displacement of these plots of Fig. b from the origin is more pronounced. The symmetry of the hydroxide and thiophenoxide lines about the line of slope 0·5 passing through the origin is, however, fictitious owing to the constant error of $0 \cdot 08 \times 10^{-3}$ g.-atom in the determination of potassium (see the Experimental section). It was thought that the presence in solution of the reactive phenyl anion might encourage side reactions with the thioanisole; search, however, failed to reveal products other than those mentioned in Table 1. Reaction in benzene is never complete as the metal acquires an insoluble coating of thiophenoxide which is only slowly abraded by stirring.

Despite the lower precision of the measurements the slope of the line for methane evolution differs significantly from that observed with dimethoxyethane. This could be accounted for by postulating ~10% radical cleavage in this solvent and assuming, as observed by Levy *et al.*,[7] that only 25% of the methyl radicals abstract protons while the remainder form " addition products." The expected stoicheiometry for reaction according to this scheme is in Table **3** and agrees with that observed within experimental error.

It is concluded that the reaction of thioanisole with potassium in the four solvents studied is mainly a two-electron cleavage. In benzene, however, and to a smaller extent in dimethoxyethane, it is possible that a small percentage of reaction proceeds by a one-electron radical mechanism.

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[6] McBay, Tucker, and Milligan, *J. Org. Chem.*, 1954, **19**, 1003.
[7] Levy, Steinberg, and Szwarc, *J. Amer. Chem. Soc.*, 1954, **76**, 3439.

EXPERIMENTAL

Reactions were carried out in an atmosphere of pure dry nitrogen. The ethers (Fluka "purum") and the aromatic hydrocarbons (Merck "pro analysis") were distilled under nitrogen after having been refluxed over potassium. Thioanisole (Fluka "purum") was distilled before use (75°/12 mm.; n_D^{20} 1·5863). Potassium (Merck) was pulverised in the appropriate solvent. The reaction mixtures were stirred magnetically and glass chips added to remove the potassium thiophenoxide from the metal surface. Analyses by gas–liquid chromatography were carried out on a Perkin-Elmer 116H Fraktomer, the gases being separated on a column of silica gel (Perkin-Elmer J) or molecular sieve (Perkin-Elmer I). Potentiometric titrations were performed on a Radiometer titrimeter with a glass electrode.

Qualitative Observations.—(i) *Reaction in* 1,2-*dimethoxyethane.* Potassium (6×10^{-3} g.-atom) and thioanisole (3×10^{-3} mole) were stirred together in dimethoxyethane (18 ml.), and the methane was collected over mercury. After 3 hr. 80% of the potassium had reacted; the mixture was then hydrolysed with water and extracted with ether. The dried extracts were fractionated at atmospheric pressure, leaving a small residue of thioanisole, and the fractions were examined by gas–liquid chromatography. Apart from thioanisole, dimethoxyethane, and ether, only methanol was detected. The aqueous layer was titrated potentiometrically against 0·1N-hydrochloric acid and showed only two waves, corresponding to hydroxide and thiophenoxide ions. Gas chromatography of the ether extract of the acidified aqueous phase showed the presence of only thiophenol. Methyl vinyl ether (b. p. 9—10°) was not observed directly but its presence was demonstrated in a separate experiment by cooling the final reaction mixture to −10°, filtering off the potassium thiophenoxide, and to the filtrate at −10° adding dropwise a solution of bromine in chloroform. After removal of most of the solvent at atmospheric pressure the residue was distilled, to yield a fraction, b. p. 55—58°/18 mm., n_D^{20} 1·5126 [1,2-dibromoethyl methyl ether has b. p. 56—58°/20 mm., n_D^{20} 1·5130 (ref. 8)].

(ii) *Reaction in diethyl ether.* Only the evolved gases were analysed by gas–liquid chromatography.

(iii) *Reaction in benzene.* With the same quantities of reactant and solvent as in (i), after 3 hr. only 60% of the metal had reacted and evolution of methane had become extremely slow. The mixture was worked-up as above and the fractions were examined by gas–liquid chromatography. Apart from an unidentified fraction (<1% of the thioanisole) appearing just before benzene, only starting materials were present. The aqueous phase contained only hydroxide and thiophenoxide anions. To demonstrate the presence of the phenyl anion, thioanisole (0·06 mole) and potassium (0·120 g.-atom) in benzene (150 ml.) were allowed to react for 2½ hr., 0·031 mole of methane being evolved. The mixture was poured on solid carbon dioxide, and unused potassium decomposed by t-butyl alcohol. Water was added, the aqueous phase separated, the thiophenoxide oxidised with aqueous 0·5N-iodine at pH 5—6, and the resultant diphenyl disulphide (0·0043 mole; m. p. 61°) removed by ether-extraction. The aqueous phase was concentrated under vacuum to one-half its original volume, acidified to pH 3—4 and extracted with ether, yielding 1·7 g. of a red viscous oil. Benzoic acid (0·003 mole) was extracted from this by sublimation, leaving an unidentified red powder, slightly soluble in hot water and completely soluble in sodium carbonate solution with the evolution of carbon dioxide. If 1 mole of phenyl anion accompanies each mole of methane, this represents a 10% yield of benzoic acid. By the carboxylation of the product of reaction between ethylpotassium and benzene, Bryce-Smith obtained a 25% yield of benzoic acid.[9] Fractionation of the organic phase yielded thiophenol (0·025 mole), diphenyl disulphide (0·001 mole), and thioanisole. No resinous residue remained.

(iv) *Reaction in toluene.* In a flask whose base terminated in a tap separated from the main vessel by a sintered-glass disc (porosity 3), thioanisole (0·025 mole) and potassium (0·05 g.-atom) were allowed to react in toluene (100 ml.). As the reaction is exothermic the flask was cooled by a current of cold air. After 15 min. a red precipitate appeared and rapid evolution of methane occurred. After 3½ hr. 98% of the methane had been evolved. The toluene was filtered off and distilled, leaving a residue (50 mg.) of unpleasant odour, which does not crystallise at −10° even on addition of bibenzyl [when a solution of bibenzyl (91 mg., 0·005 mole) in

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[8] Favorskii and Shostakovskii, *J. Gen. Chem.* (*U.S.S.R.*), 1943, **13**, 1 (*Chem. Abs.*, 1944, **38**, 330).

[9] Bryce-Smith, *J.*, 1953, 861.

toluene (100 ml.) was distilled under the same conditions, 80% of the dibenzyl was recovered, crystallising at −10° after seeding].

The benzylpotassium remaining on the sintered disc was separated from the potassium thiophenoxide by elution with dimethoxyethane, the red solution cooled in acetone–carbon dioxide, and solid carbon dioxide was added. The colourless precipitate of potassium phenylacetate (3·5 g.) was filtered off, dried, and washed with ether. The acid was obtained by neutralisation with an overall yield of 70%. Potassium thiophenoxide (0·2 g.) was recovered from the dimethoxyethane after removal of the potassium phenylacetate.

Quantitative Determinations.—A flask was attached by a capillary side-arm to a gas-burette filled with mercury. Either a standard stopper or a tap-funnel was fitted to this flask. The apparatus was kept at 20° ± 0·1°. Potassium was melted under nitrogen in dimethoxyethane, and the resulting clean metal dried *in vacuo*, weighed under nitrogen, pulverised by shaking it in the appropriate solvent, and rapidly transferred to the flask with the solvent. Any residue not transferred was decomposed with methanol and determined titrimetrically.

Thioanisole was weighed in a small glass capsule which was then suspended on a small platinum hook fused to the flask. Rotation of the stopper (to which was fused a small platinum arm) then removed the capsule from the hook and caused it to fall into the solvent.

The volume of methane evolved was read at the end of the reaction and corrected to standard temperature and pressure. Unused potassium was determined by decomposition with 9 : 1 propan-2-ol–water, introduced through the tap-funnel. The probable error in the determination of potassium was $\pm 0{\cdot}09 \times 10^{-3}$ g.-atom. The change in vapour pressure produced by the addition of alcohol introduces a systematic error such that the observed values for potassium are on the average too small by $0{\cdot}08 \times 10^{-3}$ g.-atom. This correction was not introduced as it does not change the slope of the regression line. All measurements were carried out with the same volume (18 ml.) of solvent.

After destruction of the excess of potassium the reaction mixture was transferred to a graduated flask and made up to 50 ml. with 1 : 1 propan-2-ol–water. The hydroxide and thiophenoxide ions were determined immediately by potentiometric titration with aqueous 0·1N-hydrochloric acid. Separation of hydroxide and thiophenoxide ions was better if each sample was further diluted with propan-2-ol. Tests on known mixtures of thiophenol and potassium hydroxide showed that the effects of carbon dioxide and air were negligible if the titration was performed within 2 hr. of the end of the reaction; and in both benzene and dimethoxyethane, two parallel iodometric determinations of thiophenol gave results identical with the potentiometric method within experimental error.

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