837. *Blue " Solutions " of Potassium in Ethers.*

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The properties of the blue " solutions " obtained when potassium mirrors are in contact with either pure dimethoxyethane or tetrahydrofuran have been investigated. Such " solutions " have absorption maxima at 7000 and 10,000 Å, have no detectable paramagnetism, but are conducting (specific conductivity $\simeq 10^{-5}$ mho at −78° c). They are partially decolorised by heat or by irradiation with *X*- or γ-rays, and this colour loss can be completed by centrifugation. Centrifugation and Tyndall-beam experiments indicate that the thermal ageing is accompanied by the separation and growth of solid particles. The dimethoxyethane solutions initiate anionic polymerisation of vinyl monomers but only $\simeq 30\%$ of the dissolved potassium gives rise to species capable of initiation. The concentration of the initiating species is proportional to the optical density at 7000 Å of the homogeneous solution and completely colourless " solutions " cannot initiate polymerisation, and have negligible electrical conductivity. The relevance of these and related observations to the hypothetical constituents of such solutions is discussed.

Alkali metals readily form blue solutions in ammonia and amines which are thought to possess electronic orbitals of large size and low energy, some of which are occupied by single electrons and others by pairs of electrons.[1-3] Very unstable solutions having a similar blue colour have been reported when various alkali metals interact with water [4] or alcohol [4,5] under suitable conditions. Down, Lewis, Moore, and Wilkinson [6] have recently described blue solutions which are of stability intermediate between these extremes and are formed when certain ethers are brought into contact with potassium or potassium–sodium alloys. The present work was begun with the triple object of discovering (*a*) whether the blue solutions of potassium in 1,2-dimethoxyethane (DME) or tetrahydrofuran (THF) contained solvated electrons either as " dimers " (e_2) or " monomers " (e_1), (*b*) whether they could be used as rapid initiators of anionic polymerisation, and (*c*) whether they could serve as " scavengers " of free radicals produced in the radiolysis of these ethers in the same manner as the electrons in solutions of sodium in liquid ammonia.[7] In this paper we report certain physical and chemical properties of these systems which are relevant to (*a*). Several of our findings correspond well with those reported very recently by Cafasso and Sundheim.[8]

Experimental

Preparation of Blue " Solutions."—The oils contained in freshly cut small cubes of potassium were removed by immersion in n-hexane and in pure ether for long periods. Immediately before a solution was made, one such cube was scraped under ether, removed to a baked-out glass vacuum-apparatus, and further purified by melting, decantation from any infusible solid and twice distilled *in vacuo* with complete exclusion of mercury vapour, the final distillate being in mirror form. The requisite amount of rigorously purified and degassed tetrahydrofuran or 1,2-dimethoxyethane was condensed on to the mirror at −78°, and the whole was again exhaustively degassed at −196°. After a contact time at room temperature of 5 min. for dimethoxyethane and 20 min. for tetrahydrofuran, the resultant blue liquid was decanted through a sintered-glass filter into the appropriate vessel. Longer contact periods did not cause more potassium to dissolve.

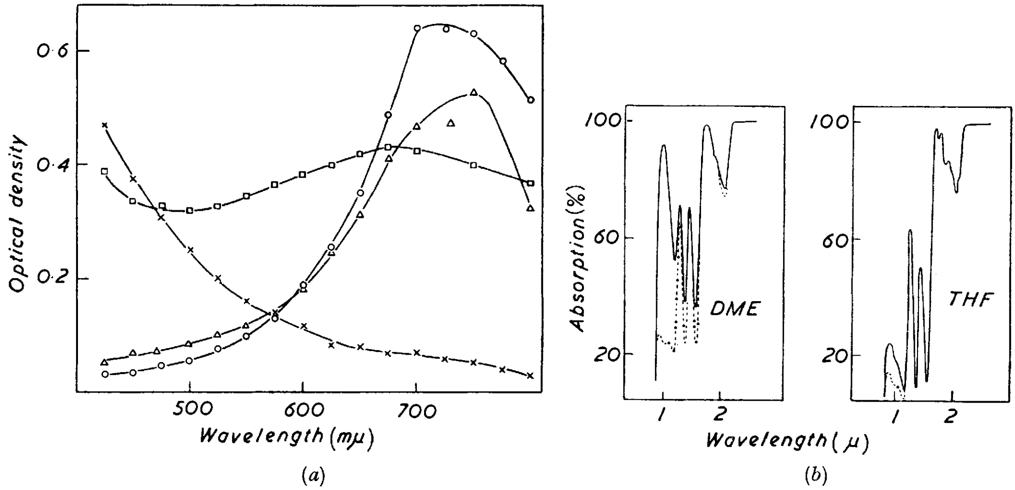
[1] Kraus, *J. Chem. Educ.*, 1953, **30**, 83.
[2] Hutchinson and Pastor, *Rev. Mod. Phys.*, 1953, **25**, 285.
[3] Symons, *Quart. Rev.*, 1959, **13**, 99.
[4] Woltorn and Fernelius, *J. Amer. Chem. Soc.*, 1934, **56**, 1551.
[5] Jortner and Stein, *Nature*, 1955, **175**, 893.
[6] Down, Lewis, Moore, and Wilkinson, *Proc. Chem. Soc.*, 1957, 209; *J.*, 1959, 3767.
[7] Cleaver, Collinson, and Dainton, *Trans. Faraday Soc.*, 1960, **56**, in the press.
[8] Cafasso and Sundheim, *J. Chem. Phys.*, 1959, **31**, 809.

The middle fraction (b. p. range 0·5°) of the ether obtained by distillation from sodium at atmospheric pressure was degassed and twice distilled *in vacuo,* being finally collected in a receiver coated with a potassium film, whereupon a blue colour usually developed Before use it was distilled on to a second mirror of purified potassium and allowed to remain for $\nless$48 hr.

Monomer Purification.—The purification [9] and use [10] of the styrene are described elsewhere.

Examination of the Solutions.—The colours of the " solutions " gradually fade and a greyish-black solid separates which is much paler when dry. The fading was assessed spectroscopically

FIG. 1. *Absorption spectra of freshly prepared " solutions " of potassium in ethers. Potassium concentrations were estimated flame-photometrically.*



(*a*) (*b*)

(a) *In the wavelength range* 400—800 mμ.

△ DME–potassium concentration = 0·5 mM.

○ DME spectrum of " solution " used to obtain previous curve remeasured after the " solution " had been cooled to −196°, then warmed rapidly to room temperature again.

□ THF–potassium concentration = 0·2 mM.

× THF after 33 min. 50 kvp *X*-irradiation and 12 min. centrifugation. Initial potassium concentration = 0·3 mM. Absorption $\lambda < 600$ mμ due to coloration of glass by *X*-irradiation.

(b) *In the infrared region.*

DME–potassium concentration = 1·0 mM.
Spectrum measured (——) 6 or (– – – –) 35 min. after preparation of " solution."
THF–potassium concentration = 0·3 mM.
Spectrum measured (——) 8 min. or (– – – –) 6 hr. after preparation of " solution."

in the wavelength ranges 350—800 mμ and 1—3 μ. The total potassium contents of completely faded " solutions," all of which were several days old and contained a very small amount of the finely divided solid, were measured by standard flame-photometric methods. The separation of this solid was accelerated by centrifugation. Studies were also made of the first appearance of the solid and its sedimentation in the gravitational field by observations of the Tyndall beam.

There was evidence that a small amount of a gas, non-condensable at −196°, was always produced during the formation of a blue " solution," and was followed by the slower evolution of a gas non-condensable at −110°. In order to identify this gas, about 15 ml. of the ether were distilled successively into three bulbs each containing a fresh potassium mirror, the solvent being in contact with only one of the mirrors at any time. Each bulb was cooled to −110°

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[9] Colclough and Dainton, *Trans. Faraday Soc.*, 1958, **54**, 886.

[10] Dainton, Wiles, and Wright, *J. Polymer Sci.*, 1960, in the press.

and any gas non-condensable at this temperature, where the vapour pressure of the ether was negligible, was collected and analysed mass-spectrometrically.

Fading of the " solutions " was greatly accelerated by irradiation with X- or γ-rays. Standard irradiation and dosimetric techniques for ^{60}Co γ-rays and 50 kvp X-rays were used.

Samples of many " solutions " were examined for paramagnetism in a standard Goüy balance assembly, and other samples contained in sealed, thin-walled, " Spectrosil " brand, high-purity, quartz tubes were placed in the resonance cavity of a Varian electron spin resonance spectrometer operating at 9400 Mc./sec. with a resonant field of 3200 gauss provided by a Mullard electromagnet and capable of detecting 10^{-9} mole $l.^{-1}$ of NN'-diphenylpicrylhydrazyl. These measurements were made at various temperatures in the range −196° to 20° and at all of which the experimental arrangement permitted the sample to be illuminated by an intense beam of unfiltered light from a Mazdalux MED-5 lamp.

The conductivities of " solutions " of various temperatures and ages were measured in a simple vacuum conductivity cell with platinum wire electrodes, which had been standardised with a potassium chloride solution.

Results

Ultraviolet, Visible, Infrared, and Electron Spin Resonance Spectra and Magnetic Properties.—Freshly prepared filtered solutions of potassium in 1,2-dimethoxyethane and tetrahydrofuran have absorption maxima at 7000 and 7200 Å respectively and also at 10,000 Å (see Fig. 1). The extinction coefficients based on the total potassium content of the solutions were ε_{7000} (DME) = ε_{7200} (THF) $(5 \pm 1) \times 10^3$ l. mole^{-1} cm.$^{-1}$.

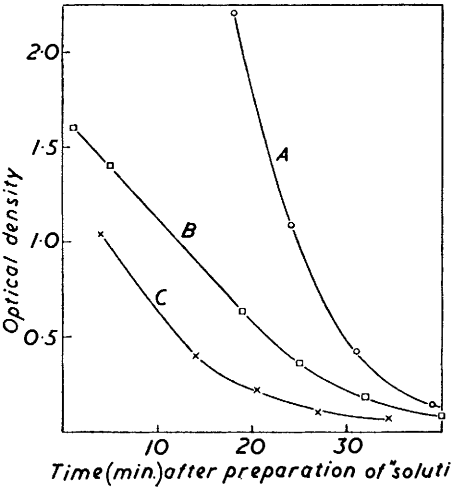


FIG. 2. *Spontaneous decay at room temperature in the absorption at* 520, 700, *and* 1000 mμ *of a freshly prepared and filtered " solution " in* 1,2-*dimethoxyethane containing potassium initially at* 1·0 mM *concentration.*

A, 700 mμ. *B*, 520 mμ. *C*, 1000 mμ.

No electron spin resonance signal was obtained from a filtered or unfiltered " solution " in each ether either in the solid or in the liquid phase, irradiated or unirradiated with ultraviolet light at any of the five temperatures specified. The sensitivity of the equipment was such that unless unusually extensive line-broadening was occurring, a spin concentration of 10^{-7}M could have been detected. A dilute ($\sim 10^{-3}$M) solution of sodium in liquid ammonia placed in the same apparatus gave the characteristically narrow and intense signal. Goüy-balance measurements at room temperature confirmed that neither dimethoxyethane nor tetrahydrofuran " solutions " are paramagnetic.

Spontaneous and Induced Changes in the " Solutions."—The solubility of potassium in dimethoxyethane at −78° is 6—10 × 10^{-4}M, which is approximately twice its value in tetrahydrofuran, and consequently saturated " solutions " in the former were a darker blue immediately after preparation. The fading of the blue colour was accompanied by diminution of absorption at 5200 and 10,000 Å (Fig. 2).

The dimethoxyethane " solutions " faded much more rapidly than those in tetrahydrofuran. The fading of both " solutions " was accompanied by formation and eventual precipitation of a dark grey powder. In a Tyndall-beam experiment on a typical dark blue dimethoxyethane " solution," no Tyndall cone was visible until 15 min. had elapsed, by which time only a slight fading was perceptible. The intensity of the scattered light increased for a further 95 min., at which the " solution " was completely colourless. Suspended particles were observed in the light beam for the following 4 days, but they had completely settled out 128 hr. after preparation of the " solution." On the assumption that the viscosity of the dimethoxyethane is 5×10^{-3} poise and that the particles had a density of 0·87 g. cm.$^{-3}$ and were spherical, their mean diameter was calculated to be of the order of 1000 Å. This result suggested that some of the blue colour of the " solutions " was due to light scattering by colloidal particles, and this conclusion was confirmed by the observation that centrifugation of an aged " solution " caused an immediate decrease of the optical density at 7000 Å to a nearly constant value (see Fig. 3). For a typical tetrahydrofuran " solution " the size of the largest particles, calculated from the sedimentation rate and on the assumptions that the particles are spherical and of density 0·9 g. cm.$^{-3}$, was found to be roughly 5000 Å. In marked contrast to these observations, centrifugation had *no* effect on the optical density of a solution of sodium in liquid ammonia which remained stable for more than 3000 hr. Microanalysis of the solids collected from a large number of bulbs in which dimethoxyethane or tetrahydrofuran was stored over excess of potassium for about 24 hr. indicated that, if due allowance is made for the possible formation of potassium carbonate during combustion, the empirical formulæ of the residues are: $(CH_2{\cdot}OMe)_2,KO_2C_2H_4$, and C_4H_8O,KOC_2H_4. During formation, both " solutions " evolved small amounts of hydrogen and hydrocarbons. In the case of 1,2-dimethoxyethane, methane comprises 96% of the hydrocarbons, and in the case of tetrahydrofuran, ethylene is by far the largest constituent. The data for tetrahydrofuran suggest that potassium induces the decomposition of the solvent into ethylene and ethylene oxide, that this oxide is polymerised, and that the polymer forms an insoluble complex with potassium. The presence of methane in the gases evolved from dimethoxyethane " solutions " suggests the possible generation of methyl radicals as precursors of the methane. Although it is not profitable to speculate further concerning these reactions, which are undoubtedly very complex, they probably have the important consequence that they yield products capable of sequestering the potassium in an insoluble form and thereby contributing to the " ageing " process.

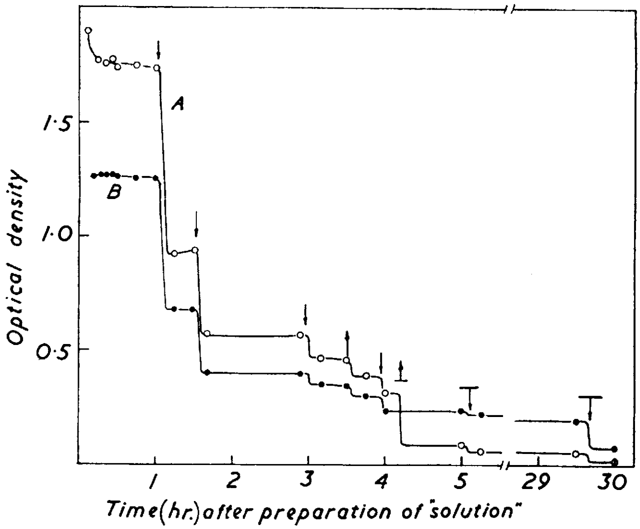


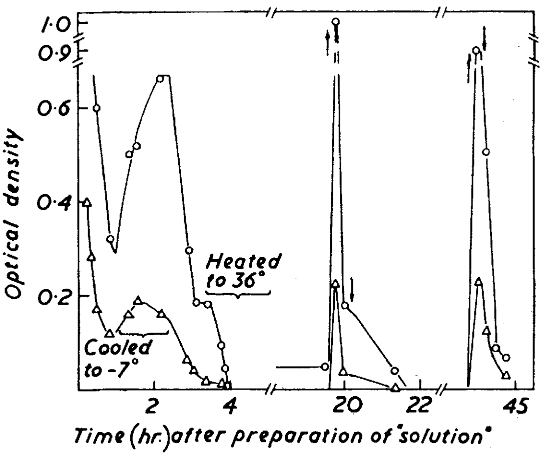
FIG. 3. *The effect of centrifugation and* X-*irradiation of a* 0·3 mM " *solution* " *of potassium in tetrahydrofuran on the optical density at* (*A*) 520 *and* (*B*) 700 mμ.

↓ Centrifuged for 5 min.
↧ „ „ 7 „
↑ Irradiation with 50 kvp *X*-rays for 3 min.
↥ Irradiation with 50 kvp *X*-rays for 30 min.

Irradiation with ^{60}Co γ-rays or 50 kvp *X*-rays caused a sudden permanent decrease of the optical density at 7000 Å (see Fig. 3), and a dose of 5×10^4 of γ-rays sufficed to bleach a solution initially 1·0 mM in potassium. However, if undissolved potassium was present the colour returned within 20 min. of cessation of the irradiation. Even in the absence of undissolved potassium repeated irradiations never reduced the optical density to zero. Only a combination of irradiation and centrifugation accomplished this rapidly. The curve -x- of Fig. 1 (*a*) shows the development of an ultraviolet absorption band during irradiation. This was due solely to radiation-induced coloration of the glass walls of the reaction vessels. A reduction in temperature of a blue " solution " always caused marked intensification of the blue colour, and spectrophotometric studies indicated that this occurred without any marked change in shape of the absorption band centred at 7000 Å. An increase in temperature of as little as 15° above room temperature caused a decrease in colour and greatly accelerated the fading. Partial restoration of colour and resumption of the characteristic fading rate were achieved when the solution was brought back to room temperature. A greater degree of restoration of colour was obtained if either solid potassium was present or the solution was poured on to a fresh potassium surface. Cooling a " solution " to −78° caused a very large increase in colour, and this deeper blue lasted for many minutes after the " solution " had been brought back to room temperature [cf. Fig. 1 (*a*)]. This phenomenon was observed many times in both the presence and the absence of a potassium mirror, although restoration of colour of a completely bleached " solution " necessitated contact with a fresh potassium surface. Some of these effects are shown in Fig. 4.

FIG. 4. *The effect of changes of temperature on the optical densities at* 520 *and* 700 mμ *of a* 1,2-*dimethoxyethane " solution " of potassium in contact with excess of metal.*

○ 700 mμ. Δ 520 mμ. ↑ cooled to −196°, then warmed rapidly to room temperature. ↓ Centrifuged for 7 min.



Changes in Specific Conductivity.—At −78° the specific conductivity of a blue " solution " of 1 × 10^{-3} mole of potassium per litre of 1,2-dimethoxyethane was 7·8 × 10^{-6} mho. Fading of the " solution " either occurring spontaneously or brought about by warming caused a decrease in the specific conductivity, and when the colour was no longer visible the specific conductivity had fallen to the constant value of 7 × 10^{-9} mho. At a potassium concentration of 0·2mM the equivalent conductivity at room temp. is ~20 mho^{-1} cm.^2, a result which suggests that considerable ion-pairing is taking place even at this dilution.

Concentration of Polymerisation Initiating Species.—The addition of styrene to blue " solutions " of potassium in dimethoxyethane caused the formation of red " living " polystyrene.[10] The polymerisation being assumed to proceed by the anionic mechanism proposed by Szwarc *et al.*,[11] the number of initiating species could be equated to twice the number of polystyrene molecules formed. The results indicated that only 30% of the total potassium content of a fresh, saturated, 1,2-dimethoxyethane " solution " was effective as initiator. " Solutions " which had become completely bleached either by heat or by γ-irradiation did not initiate polymerisation, and experiments with partially faded " solutions " showed that the concentration of active species was proportional to the optical density at 7000 Å. A freshly prepared filtered " solution " kept at −78° showed no detectable change in colour or concentration of initiating species during 3 days.

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[11] Swarc, Levy, and Milkovitch, *J. Amer. Chem. Soc.*, 1956, **78**, 2656.

DISCUSSION

Some of the experiments reported here have also been described by other investigators [6,8] and in most cases there is good agreement between the results. *E.g.*, Cafasso and Sundheim's data [8] concerning the solubility of potassium in 1,2-dimethoxyethane and the visible spectra, thermal fading, and conductivities of the resultant solutions are confirmed by our results. However, these authors did not detect the infrared band at 1 μ for potassium in this ether although they did find it for a solution of cæsium in di-[2-(2-methoxyethoxy)-ethyl] ether and they also observed near-infrared bands at 0·89 and 0·91 μ for solutions of rubidium in this solvent and our ether respectively. Cafasso and Sundheim,[8] in common with ourselves and others,[12] obtained no paramagnetic resonance absorption in liquid potassium–dimethoxyethane systems, whereas Tuttle and Weissman [13] reported a " weak spin resonance absorption line about two oersteds in breadth." Contrary to our findings, Cafasso and Sundheim report that when solutions of potassium in dimethoxyethane are frozen a paramagnetic resonance spectrum appears which disappears abruptly on melting. No satisfactory explanation for these discrepancies can be given. Perhaps the least objectionable view would be to associate these differences with the extreme susceptibility of the alkali metal–ether systems to traces of impurities.

In spite of these inconsistencies, it is possible to compare, with some confidence, " solutions " of potassium in tetrahydrofuran and 1,2-dimethoxyethane with the true solutions of alkali metals in ammonia and amines. The electrical properties of the former are similar to those of dilute versions of the latter. The effect of temperature on the blueness of ether " solutions " is analogous to that reported for the amine systems.[14] The absence of free spins in the ether " solutions," though surprising in view of the infrared band, is in keeping with the expected gradation of properties in the series of decreasing dielectric constant from ammonia, through amines to ethers.

The absorption band, with a maximum at, or near, 7000 Å, which is also found under suitable conditions for all alkali-metal solutions, is probably attributable to species containing electrons with paired spins, which may be expanded metal dimers. It also seems possible that the 1 μ band corresponds to the absorption peak at 1·5 μ found for alkali metal–amine solutions and is due to the same species, namely, unpaired electrons in solvent cavities. On the other hand, the shifts which this band sometimes undergoes when either the solute or solvent is changed suggest that it might be due to " expanded metal monomers." Whichever hypothesis is correct, the infrared band in the ether " solution " cannot be taken as evidence for the presence of appreciable concentrations of paramagnetic species. If an equilibrium exists between the spin-paired and unpaired species the concentration of the latter cannot exceed 0·1% of the concentration of the former, and consequently the transition probability and extinction coefficient of the infrared band would be excessively large. Furthermore, the fact that illumination of solid and liquid " solutions " with intense unfiltered light from a mercury arc causes neither bleaching nor any detectable paramagnetic resonance signal strongly suggests that, if electron transfer from the dimers occurs on irradiation with ultraviolet light, as is the case with rigid glasses containing lithium and methylamine,[15] the reverse reaction must be very rapid in the solid as in the liquid phase.

The polymerisation experiments provide strong evidence that the ether " solutions " contain negatively charged species which initiate the polymerisation of styrene by donation of electrons to styrene molecules, the resulting radical ion propagating anionically. The correlation between the initiator concentration of the solutions, determined by the polymerisation technique, and their optical density at 7000 Å indicates that the initiators are

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[12] Ref. 25 of ref. 3 (not available to the authors).

[13] Tuttle and Weissman, *J. Amer. Chem. Soc.*, 1958, **80**, 5342.

[14] Fowles, McGregor, and Symons, *J.*, 1957, 3239.

[15] Berry, Linschitz, and Schweitzer, *J. Amer. Chem. Soc.*, 1954, **76**, 5833.

pairs of solvated electrons or solvated dimeric ion pairs. There appears to be no obvious reason * why the initiator concentration should be only ~30% of the total potassium concentration of the " solutions." and it is therefore necessary to assume that more than half the potassium is dispersed in the solvent in a form which makes it ineffective as an initiator (see below).

The feature which sets ether " solutions " apart from other alkali-metal solutions is the heterogeneity which develops during the decay process. The decay itself indicates that the solvated electron pairs on expanded metal dimers are unstable relative to reaction products which are evidently insoluble. The high potassium content of the residue from the aged tetrahydrofuran " solution " suggests that, during the growth of the nuclei of the products, solute and probably also solvent molecules are trapped and thereby withdrawn from true solution and deprived of their power of initiating polymerisation. Perhaps it is permissible to regard all solutions of alkali metals in liquids as potentially capable of containing a whole spectrum of entities ranging from single electron cavities through solvated expanded metal dimers to metal–solvent agglomerates; and that the most stable species differ from system to system and depend upon metal concentration within the same system, although the expanded metal dimer is a common constituent of all systems having an absorption maximum around 7000 Å.

The details of the primary act when ethers are subjected to ionising radiation are not known. However, it is very likely that amongst the products will be free radicals, such as alkoxyl radicals (RO•), the electron affinity of which will considerably exceed the binding energy either of a single electron in a solvent cavity or of an electron in the orbital of an expanded metal dimer. These latter species will therefore enter into rapid exothermic reactions exemplified by the scheme

$$\mathrm{RO}\cdot + \mathrm{e_1}^- \text{ (or } \mathrm{e_2}^{2-}) \longrightarrow \mathrm{RO}^- + \text{(or } \mathrm{e_1}^-)$$

and will thereby act as efficient " scavengers " of those radicals having sufficient electron affinity. Radiation-induced bleaching of blue potassium in ether " solution " in a manner entirely analogous to that of sodium in liquid ammonia[7] is therefore to be expected. The data of the previous section indicate the G value for such radicals is about 8 ± 2 for ^{60}Co γ-rays, a not unreasonable result for an organic ether.

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* A similar situation appears to exist when sodium–naphthalene is made. Allen and Stretch[16] have recently reported that " owing to side reactions and an incomplete primary reaction between the metal and hydrocarbon " less sodium–naphthalene is produced than total sodium used.

[16] Allen and Stretch, *Proc. Chem. Soc.*, 1959, 399.