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Decay kinetics of solvated electrons and isotope effect in the reaction of alkali metals with alcohols

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SEZIONE II
(Fisica, chimica, geologia, paleontologia e mineralogia)

Chimica. — *Decay kinetics of solvated electrons and isotope effect in the reaction of alkali metals with alcohols.* Nota di IGNAZIO RENATO BELLOBONO (*) e MARIO TURI CATALDI (**), presentata (***) dal Socio G. SARTORI.

RIASSUNTO. — È stata studiata, a 25 °C, la cinetica della reazione fra Li, Na, K, Rb, Cs e gli alcooli ROD ($R = CH_3, C_2H_5, n\text{—}C_3H_7, i\text{—}C_3H_7$). Sono stati parimenti misurati gli effetti isotopici in miscele di alcooli deuterati e non deuterati, in funzione della percentuale in volume di ROH nella fase liquida. Il fattore di separazione isotopica $(H/D)_{gas}/(H/D)_{liquido}$ è stato trovato costante ($2{,}0 \pm 0{,}25$ a 25 °C), nei limiti dell'incertezza sperimentale, ed indipendente sia dal tipo di metallo alcalino, che dal tipo di alcool. Nelle condizioni di stazionarietà, combinando la teoria della diffusione con la cinetica chimica omogenea, si sono valutate le costanti di velocità che risultano compatibili con lo schema (1)–(3 b). Anche gli effetti isotopici si accordano soddisfacentemente con tale meccanismo e confermano l'intervento di un dimero dell'elettrone solvatato, la cui formazione è all'origine dell'effetto isotopico osservato.

Chemical evidence that the electron is an intermediate in the reaction of sodium with alcohol was first reported by Bennett *et al.* [1, 2]. Reaction kinetics of sodium with liquid methanol and ethanol was subsequently studied by Fletcher and Richards [3]. The mechanism with an alcohol deuterated in the oxy position may be generalized as follows:

$$\text{(1)} \qquad Me + mC_nH_{2n+1}OD \rightarrow e^- (C_nH_{2n+1}OD)_m + Me^+$$

$$\text{(2)} \qquad e^- (C_nH_{2n+1}OD)_m + C_nH_{2n+1}OD \xrightarrow{k_2}$$

$$\xrightarrow{k_2} HD + mC_nH_{2n+1}OD + C_nH_{2n}DO^-$$

$$\text{(3a)} \qquad e^- (C_nH_{2n+1}OD)_m + e^- (C_nH_{2n+1}OD)_m \xrightarrow{k_3}$$

$$\xrightarrow{k_3} e^- (C_nH_{2n+1}OD)_2 + (2m - 2) C_nH_{2n+1}OD$$

$$\text{(3b)} \qquad e^- (C_nH_{2n+1}OD)_2 \rightarrow D_2 + 2\, C_nH_{2n+1}O^{-}.$$

In the absence of electron scavengers two modes of electron decay are possible, either pseudo-first order decay (2) or bimolecular recombination (3a) followed by (3b). The analogy between the reaction occurring in aqueous solution [4] and that in alcoholic media has been shown [3].

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In the present paper the mechanism (1)-(3b) was investigated, with the particular aim of ascertaining whether reaction (1) was indeed faster than reactions (2) and (3b), the rates of which were measured, to study the possible influence of the alcohol, and to examine particularly the origin of isotope effects, as well as their magnitudes with different alcohols.

RESULTS AND DISCUSSION

The stoicheiometry of the reaction

$$2\ \mathrm{Me}\,(s) + 2\ \mathrm{ROH}\ (\mathrm{D}) \rightarrow 2\ \mathrm{Me}^{+}\,\mathrm{RO}^{-} + \mathrm{H}_2\ (\mathrm{D}_2\ ,\ \mathrm{HD})\ (g) \tag{4}$$

was studied at 25 °C with $\mathrm{Me} = \mathrm{Li}, \mathrm{Na}$ and K, and $\mathrm{R} = \mathrm{CH}_3, \mathrm{C}_2\mathrm{H}_5$, n—$\mathrm{C}_3\mathrm{H}_7$, and i—$\mathrm{C}_3\mathrm{H}_7$, in mixtures of deuterated and non deuterated alcohols, as a function of the volume percent of ROH in the liquid phase. The results are reported graphically in fig. 1. As can be observed, there is no difference in results, beyond the experimental uncertainty, on changing the alcohol or the alkali metal. When using the 99.5-99.7 % deuterated alcohols $\mathrm{CH}_3\mathrm{OD}$, $\mathrm{C}_2\mathrm{H}_5\mathrm{OD}$, and i—$\mathrm{C}_3\mathrm{H}_7\mathrm{OD}$, with Na, Li, and K, the hydrogen formed

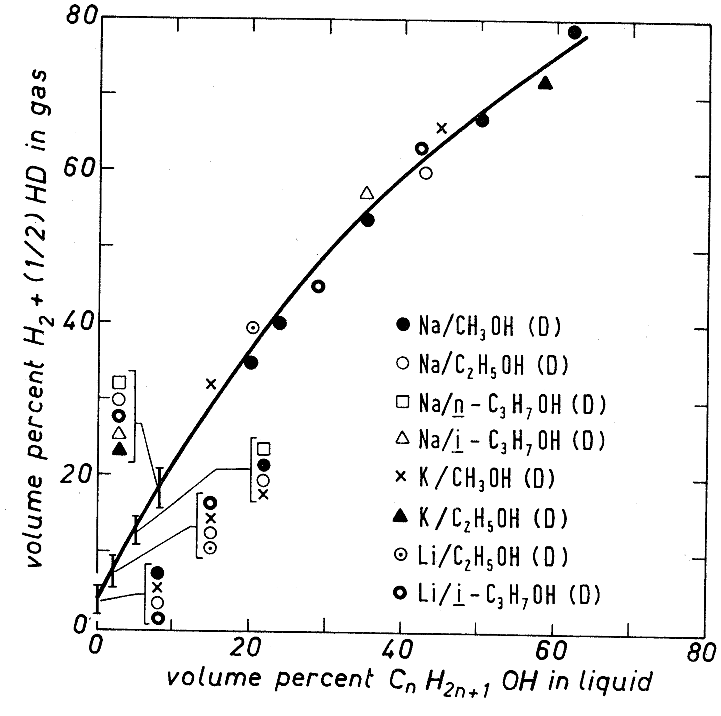

Fig. 1. – Volume percent of protium ($\mathrm{H}_2 + (1/2)\,\mathrm{HD}$) in the gas phase, as a function of volume percent of $\mathrm{C}_n\mathrm{H}_{2n+1}\mathrm{OH}$ in the liquid phase (mixtures of alkanols deuterated and not deuterated at the oxy position), in the reaction of alkali metals with alcohols, at 25 °C, under steady state conditions.

contained 95.5 ± 0.8 % of deuterium, 0.3 ± 0.2 % of protium, and 4.2 ± 1.2 % of HD, mainly as a consequence of the pseudo-first order reaction (2). The rate constant k_2 of this reaction does not seem to be consequently much affected by the molecular weight of the alcohol, at least for the C_1—C_3 alcohols tested. When taking into account the formation of HD by this reaction, all the experimental points fit satisfactorily well the curve of fig. 1, calculated by assuming an isotope effect (defined as the ratio of H/D in the gaseous hydrogen formed to the oxy H/D in the solvent mixture) independent of the composition of the solvent and equal to the constant value 2.0. Experimental points deviate from this value by no more than ± 0.25.

TABLE I

Reaction rates under steady state conditions and rate constants (k_3) *of reaction* (3a), *for the dissolution of alkali metals in various alcohols, at* 25 °C (1).

	CH_3OD		C_2H_5OD	
	N_A (gmole sec^{-1} cm^{-2})	k_3 (M^{-1} sec^{-1})	N_A (gmole sec^{-1} cm^{-2})	k_3 (M^{-1} sec^{-1})
Li . . .	$(9.6\pm0.8)\ 10^{-6}$	$(4.4\pm1.0)\ 10^{9}$	—	—
Na . . .	$(10.8\pm0.9)\ 10^{-6}$	$(3.9\pm0.9)\ 10^{9}$	$(4.6\pm0.6)\ 10^{-6}$	$(6.5\pm1.0)\ 10^{9}$
Na (2) . .	10×10^{-6}	$(3.3\pm2.0)\ 10^{9}$	4×10^{-6}	$(7\pm3)\ 10^{9}$
K . . .	$(10.2\pm0.9)\ 10^{-6}$	$(4.1\pm0.8)\ 10^{9}$	$(5.2\pm0.8)\ 10^{-6}$	$(5.9\pm0.9)\ 10^{9}$
Rb . . .	$(9.9\pm1.0)\ 10^{-6}$	$(4.3\pm0.7)\ 10^{9}$	$(4.1\pm0.7)\ 10^{-6}$	$(6.3\pm0.8)\ 10^{9}$
Cs . . .	$(11.2\pm1.1)\ 10^{-6}$	$(3.8\pm0.9)\ 10^{9}$	—	—

	n—C_3H_7OD		i—C_3H_7OD	
	N_A (gmole sec^{-1} cm^{-2})	k_3 (M^{-1} sec^{-1})	N_A (gmole sec^{-1} cm^{-2})	k_3 (M^{-1} sec^{-1})
Li . . .	—	—	$(5.6\pm1.0)\ 10^{-7}$	$(4.3\pm0.8)\ 10^{10}$
Na . . .	$(2.1\pm0.6)\ 10^{-6}$	$(1.1\pm0.3)\ 10^{10}$	$(6.2\pm1.2)\ 10^{-7}$	$(3.6\pm1.3)\ 10^{10}$
Na (2) . .	—	—	—	—
K . . .	—	—	—	—
Rb . . .	—	—	$(6.9\pm1.5)\ 10^{-7}$	$(3.3\pm1.1)\ 10^{10}$
Cs . . .	$(1.9\pm0.8)\ 10^{-6}$	$(1.0\pm0.4)\ 10^{10}$	—	—

(1) Uncertainties are standard deviations.
(2) Reference [3].

Since the kinetics of reaction (4) occurs at or near the surface of the alkali metal and consequently involves spatial inhomogeneity, for the calculation or reaction specific rates, the same mathematical treatment was applied as that derived by Fletcher and Richards [3]. The results are reported in Table I, together with the experimental steady state reaction rates (N_A, gmole $sec^{-1} cm^{-2}$) for the dissolution of the alkali metals in the various deuterated alcohols. For obtaining k_3 values of Table I, a value of $k_2 = 1.1 \times 10^5 sec^{-1}$ was adopted [3] and was considered to be independent of the alcohol and of the alkali metal. Even if this may not be rigorously true, it may be observed that values in CH_3OD and C_2H_5OD are in fact very close [3], and in any case rate constants of reaction (2), being a protium abstraction from the alcohol by the solvated electron, must not be markedly influenced by the alkyl group. Results of Table I clearly indicate that the rate of dissolution reaction is independent of the alkali metal. This fact, together with the non-dependency of the isotope separation factor on the alkali metals, is consistent with a scheme (1)-(3*b*) requiring that reaction (1) be faster than the parallel reactions (2) and (3 a).

The calculated rate constants k_3 may be interpreted [3] as corresponding to the formation of a solvated dimer (reaction (3 *a*)). The transition state of this reaction would have to have a lifetime long enough to allow preferential cleavage of the OH over the OD bonds of the solvated molecules, and this should be the origin of isotope effects. The nearly double isotope separation factor for the analogous reaction in water [5] may arise from another additional isotope effect in reaction (3b), which is impossible with an alcohol, since in the latter case there are only two available hydrogens per dimer.

The values of k_3 for the reaction with the alkanols increase with decreasing basicity of the alkoxide ions, as expected, towards the limiting value of diffusion control for reaction (3a), which is almost reached in water. This fact is also consistent with the proposed reaction mechanism (1)-(3b).

It has been suggested [6, 7] that the potential well of the electron in water is based on a tetrahedral arrangement of four water molecules. The electron is bound inside by electrical and orientational polarization of the water molecules at the four corners of the tetrahedron. The orientational polarization seemingly involves hydrogen bond breakage. The electron moves with a high probability by tunnelling as long as the water molecules rotate rapidly and the tetrahedral structure changes frequently. A similar model may hold in the alcoholic solution, but a solvation unity with two, instead of with four molecules, must be visualized.

EXPERIMENTAL

Analytical grade reagents were obtained from Merck (Darmstadt, BRD). Deuterated alcohols, prepared from aluminium alkoxides and 99.7-99.9 % deuterium oxide, were purified by vacuum distillation. Nuclear magnetic resonance and infrared analysis gave 99.5-99.7 % of deuterium at the oxy position. All operations were performed inside a dry box, in a purified nitrogen stream.

Kinetic measurements were carried out in a double valved side arm of a thermostatted reaction vessel, connected to a Cahn electrobalance. The resulting hydrogen was analyzed, in some instances, after freezing the alcohol, by mass spectrometry.

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