ganic acids by washing with dilute aqueous sodium carbonate and then with water, the benzene solution was allowed to evaporate at room temperature. The 0.160 g. (69%) of oxide, m.p. 66–67°, which remained was crystallized at 0° from 40–60° petroleum ether, yielding analytically pure material, m.p. 67.5–68.0°.

Anal. Calcd. for $C_6H_8Br_2O$: C, 28.14; H, 3.13. Found: C, 28.56; H, 3.28.

DEPARTMENT OF CHEMISTRY
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COMMUNICATIONS TO THE EDITOR

SALT EFFECTS ON NON-ELECTROLYTES IN PARTIALLY AQUEOUS MIXED SOLVENTS[1]

Sir:

Previous work on kinetic salt effects[2,3] had led us to the belief that salt effects on non-electrolytes in mixed, partly aqueous solvents might be quite different from corresponding effects observed in water.

This belief has been borne out by some data recently obtained from solubility measurements in 50% dioxane at 25°, as tabulated in Table I.

TABLE I

Non-electrolyte	Solvent	Salt	*k*
Benzoic Acid	Water[4]	NaCl	0.182
		HCl	.121
		KCl	.093
		KI	.041
α-Naphthoic Acid	50% Dioxane	HCl	.011
		KI	.017
		NaCl	− .12
		KCl	− .15
Naphthalene	Water[5]	NaCl	.260
		KCl	.204
	50% Dioxane	NaCl	− .09
		KCl	− .08

The data show that the salting order of various electrolytes in 50% dioxane is quite different from that generally observed in water.[3] This can be seen by comparing the values of *k* in Table I, which were obtained by plotting log $\frac{S^\circ}{S}$ versus C_S and measuring the slope. A positive *k* is associated with salting-out while a negative *k* results from salting-in of the non-electrolyte by the salts present. For example, NaCl and KCl, which in water are usually better salting-out agents than HCl and KI, in 50% dioxane actually cause salting-in.

A qualitative understanding of the effect of the mixed solvent on the salting order of electrolytes may be reached on the basis of the preferential hydration of the electrolytes. Consider, for example, the effects due to KCl. In water, hydration of KCl leaves less solvent for the non-electrolyte to dissolve in; hence, salting-out. In 50% dioxane, preferential solvation by water leaves an effective solvent richer in dioxane. When the non-electrolyte solubility increases with dioxane content, the net effect may be salting-in. The solubility data for naphthalene and α- naphthoic acid in Table II suggest this as a partial explanation.

TABLE II

Nonelectrolyte	Dioxane, %	Solubility (g./100 ml.)
α-Naphthoic Acid	40	0.89
	50	2.91
	60	7.57
Naphthalene	40	0.44
	50	0.79

The present data suggest that previous treatments of kinetic salt effects as colligative functions of ionic strength, or even on the basis of the Setschenow equation, may be oversimplified in partly aqueous solvents.

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ERNEST GRUNWALD

RECEIVED FEBRUARY 10, 1955

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[1] This paper is based on research done under contract Nonr 988(02) with the Office of Naval Research.

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AN INVESTIGATION OF THE HYPOTHETICAL ION PAIR INTERMEDIATE IN THE REARRANGEMENT OF 9-DECALYL HYDROPEROXIDE BENZOATE USING OXYGEN-18

Sir:

Recently, ion pairs have been considered as intermediates in a variety of organic reactions.[1,2,3] The degree of separation of the ions in many of these reactions, particularly those ion pairs which have been dubbed "intimate" or "internal," has remained obscure. We wish to report the results of an oxygen-18 tracer study of the rearrangement of the benzoate of 9-decalyl hydroperoxide (I), a reaction which has the properties of an intimate ion pair reaction.[4,5]

Benzoyl chloride-O^{18}, prepared from benzoic acid-O^{18}, was allowed to react with 9-decalyl hydroperoxide to form I. I was rearranged in both methanol and acetic acid to give 1-benzoyl-1,6-epoxycyclodecane (III) which was reduced with lithium aluminum hydride to benzyl alcohol

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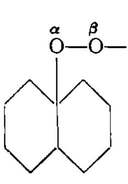
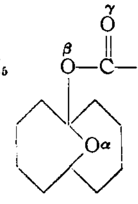
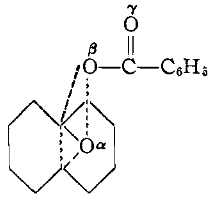

I


III


VI

(IV) and 1,6-dihydroxycyclodecane (V). Table I contains the analytical data.

TABLE I

OXYGEN-18 ANALYTICAL DATA[a]

	Atom % excess oxygen-18					
	Starting compounds		Methanol run		Acetic acid run	
Benzoic acid (II)	1.35	1.38				
Perbenzoate (I)	1.37	1.37				
Benzoate (III)			1.29	1.30[b]	1.23[b]	
Benzyl alcohol (IV)			1.16	1.17	1.19	1.20
1,6 - Dihydroxycyclodecane (V)			0.024	0.026[c]	0.012	0.014[c]

[a] Analyzed by the method of W. E. Doering and E. Dorfman, THIS JOURNAL, **75**, 5595 (1953). Normal isotopic abundance was taken as 0.204 atom % oxygen-18. [b] The diminution in oxygen-18 content in these samples probably occurred in their purification by crystallization from methanol–water, see M. Bender, *ibid.*, **73**, 1626 (1951). [c] A sample of inactive diol showed 0.204% oxygen-18.

Inspection of the data shows that no more than 2% of the excess oxygen-18 is found in the diol and the rest remains as carbonyl oxygen during the rearrangement. These results are inconsistent with the formation of an ion pair in which O^{β} and O^{γ} become equivalent,[5] and also rule out a quasi-ring transition state in which O^{γ} of I would become O^{β} of III. A very attractive explanation of these results involves a concerted shift of the benzoate group, with retention of its structural integrity in all respects, at the same time that carbon is migrating to oxygen. Such a process can be represented in terms of VI, which can be either a transition state or very short lived intermediate. A structure of the general type exemplified by VI can also be used to describe the details of other internal ion pair rearrangements.[1]

Acknowledgment.—The author wishes to thank Dr. J. E. H. Hancock for his help and advice in carrying out the oxygen-18 analyses.

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EVIDENCE FOR QUADRIVALENT CURIUM: X-RAY DATA ON CURIUM OXIDES[1]

Sir:

The preparation of several curium oxides has been carried out and their X-ray lattice constants measured. These unequivocally show the existence of an oxide with a O/Cm ratio more nearly 2/1 than 1.5/1 on the basis of lattice constants.

Cm^{244}, an alpha emitter of ~19.2 years[2] half-life, obtained from pile irradiation of Pu^{239} by the reactions $Pu^{239} \xrightarrow{n} Pu^{240} \xrightarrow{n} Pu^{241} \xrightarrow{n} Pu^{242} \xrightarrow{n} Pu^{243} \xrightarrow{\beta^-} Am^{243} \xrightarrow{n} Am^{244} \xrightarrow{\beta^-} Cm^{244}$, was used for most of the work although Cm^{242}, a 162-day emitter,[3] was used initially. The Cm^{244} was purified at Argonne National Laboratory, with 3% Ca as the only impurity present to more than 0.5% except for Am which was present in the amount of 0.8% at the time of analysis. A subsequent oxidation to Am(VI) with precipitation of the curium as curium trifluoride should have reduced the amount of Am by a factor of from 2 to 10.

In all cases, the initial preparation of the sample consisted of precipitation of curium(III) oxalate in the capillary and ignition of this compound *in situ* in an atmosphere of oxygen at ~400°. Such oxides were black in color.

With Cm^{244}, 10 micrograms of material with X-ray exposures of 20 hours were found satisfactory. With the shorter-lived Cm^{242}, it was found necessary to use $\leqslant 1/2$ microgram and exposures of <1 hour. The longer exposures were made in a 114.6 mm. diameter camera with Eastman Type A film using filtered copper radiation; the shorter exposures in a 60-mm. diameter camera with no-screen film using unfiltered copper radiation.

Curium sesquioxide was prepared by the thermal decomposition of the black oxide at 600° at 10^{-4} mm. pressure; the product was white or faint tan in color. X-Ray analysis showed it to be cubic in structure with $a_0 = 5.50 \pm 0.01$ Å. for the pseudo cube. As can be seen in Table I, this is reasonable for the compound Cm_2O_3.

TABLE I

CUBIC OXIDE XO_2, X_2O_3 COMPOUNDS

X	Lattice constants X_2O_3 (Å.), $a_0/2$	Source	Lattice constants XO_2 (Å.)	Source
U	....		5.4700 ± 0.0001 at 25°C.	F. H. E.[4]
Np			5.4341 ± 0.0002	Present work
Pu	5.52 ± 0.01	F. H. E.[4]	5.3960 ± .0003	
Am	5.515 ± .005	D. H. T.[5]	5.376 ± .001	Present work
Cm	5.50 ± .01	Present work	5.372 ± .003	

Curium oxide, black, obtained from air ignition gave $a_0 = 5.43$ Å. One oxide was prepared by treatment with an ozone–oxygen stream at 650° followed by slow cooling to 300° in the gas stream. Another oxide sample was made by heating Cm_2O_3 in 1 atm. of oxygen to 650° with slow cooling in the gas. The lattice constant obtained from these two differently treated samples was 5.372 ± 0.003 Å.

In Figure 1 the best values of the dioxides obtainable are plotted against atomic number. Redeterminations were made of NpO_2 (prepared in 1 atm. hydrogen at 1000°), PuO_2 (prepared in 1 atm. oxygen at 600° with slow cooling), and AmO_2 (prepared in a stream of ozone at 600° with slow cooling), in order to obtain accurate values of the

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[1] This work was sponsored by the U. S. Atomic Energy Commission.

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