ion.[3] The strange behavior of oxygen in these compounds has been emphasized recently by P. J. Wheatley[4] and discussed in a review paper by R. J. Gillepsie and R. S. Nyholm.[5]

Surprisingly, in the course of an X-Ray study of $[TiCl_2(C_5H_5)]_2O$[6] we found definite evidence of colinearity of titanium and oxygen atoms. In fact, the crystals of (I), having these unit cell constants: $a = 7.47$ Å.; $b = 9.86$ Å.; $c = 12.58$ Å.; $\beta = 127°56'$, space group $P2_1/c$, have only two molecules per unit cell, so that the molecule must be centrosymmetrical.

The colinearity of titanium and oxygen atoms is further confirmed by the Patterson and Fourier syntheses on the *ac* and *bc* planes. At the present stage of refinement of the structure (R = 0.20), the fractional coördinates (x, y, z) of the heavy atoms have been assumed to be: Ti: 0.454, 0.132, 0.393; Cl^{I}: 0.767, 0.132, 0.403; Cl^{II}: 0.178, 0.047, 0.187.

It results that: 1, as above said, the Ti-O-Ti atoms are colinear. 2, All the carbon atoms of the cyclopentadiene ring are at the same distance (2.35 ± 0.05 Å.) from the titanium atom. 3, Other relevant interatomic distances are: Ti-O = 1.78 ± 0.03 Å.; Ti-Cl = 2.25 ± 0.04 Å.; $Ti\text{-}C_5H_5$[7] = 2.03 ± 0.05 Å. 4 Relevant bond angles are: O-Ti-Cl = 104° ± 2°; Cl-Ti-Cl = 104° ± 2°; $C_5H_5\text{-}Ti\text{-}Cl$[7] = 112° ± 2°; $C_5H_5\text{-}Ti\text{-}O$[7] = 117° ± 2°. The Ti-O distance is clearly shorter than the one expected for a single bond (1.78 Å. instead of 1.92 Å.),[8] as was the case of the Ru-O[3] distance in the corresponding anion.

Supposing an sp hybridization for the oxygen, and a d^3s hybridization for the titanium atoms, a partial double bond character of the Ti-O bond may arise from donation of electrons from the p_y and p_z filled oxygen orbitals to the $d\gamma$ unfilled titanium orbitals. This fact may in turn stabilize the unusual sp hybridization at the oxygen atom.

We acknowledge the helpful suggestions of Prof. G. Natta, Prof. G. R. Levi and Dr. L. Porri, who also supplied us the sample.

(3) A. McL. Mathieson, D. P. Mellor and N. C. Stephenson, *Acta Cryst.*, **5**, 185 (1952).

(4) P. J. Wheatley, in "Annual Review of Physical Chemistry," **8**, 383 (1957).

(5) R. J. Gillespie and R. S. Nyholm, *Quart. Rev.*, **11**, 339 (1957).

(6) Prepared by boiling in moist air a heptane solution of $TiCl_3(C_5H_5)$. The yellow tabular crystals of $[TiCl_2(C_5H_5)]_2O$, stable in air, may be recrystallized from heptane (private communication of L. Porri).

(7) Referred to the center of the cyclopentadiene π-bonded ring.

(8) Obtained by subtracting from the found Ti-Cl distance (2.25 Å.) the difference between the covalent radii of chlorine and oxygen atoms (0.33 Å.).

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RECEIVED JULY 22, 1959

LARGE SALT EFFECTS IN NON-POLAR SOLVENTS

Sir:

Specific effects of added salts in accelerating rate of ionization of organic substrates such as alkyl toluenesulfonates tend to become quite serious in the less polar solvents, *e.g.*, AcOH.[2] In this Communication we call attention to the large magnitude of such salt effects in the poorest ionizing media and their implications for reaction mechanism.

The rate of ionization of *p*-methoxyneophyl *p*-toluenesulfonate[2b] (I) may be followed in a variety of solvents by titration of generated toluenesulfonic acid, and this is accelerated by inclusion of, *e.g.*, lithium perchlorate. With this salt, the pattern of salt effects in the 0–0.10 M range is the linear[2] one of equation (1) or the more complex one of equation (2), where k and k^0 are first order rate constants with and without added salt, respectively.

$$k = k^0[1 + b(LiClO_4)] \qquad (1)$$

$$k = k^0[1 + b(LiClO_4) + c(LiClO_4)^{3/2}] \qquad (2)$$

As summarized in Table I, such salt effects tend to become quite large in the less ionizing solvents, such as acetone, octanoic acid and ethyl acetate, and enormous in a solvent such as diethyl ether. In the latter medium, ionization rate is increased by a factor of 10^5 by 0.1 M lithium perchlorate.

Because of the large salt effects on ionization illustrated in Table I, inclusion of a salt may drastically alter relative ionizing power of solvents. The comparison between acetic acid and diethyl ether is illustrated in Fig. 1. While rate of ionization of I in acetic acid at 50° in the absence of lithium perchlorate exceeds that in ether by a factor of 2×10^4, ether becomes a better ionizing medium than acetic acid at concentrations of lithium perchlorate above 0.036 M. For S_N2 displacement reactions with salts such as lithium chloride, the choice of a relatively poor ionizing solvent may not minimize but instead can promote

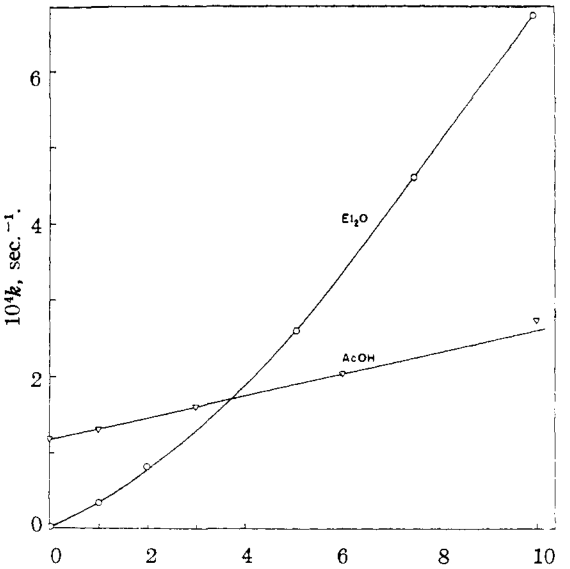

Fig. 1.—Plot of k for I in Et_2O and AcOH at 50.0° *vs.* $[LiClO_4]$.

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(1) Research supported by the National Science Foundation.

(2) (a) S. Winstein, *et al.*, THIS JOURNAL, **76**, 2597 (1954); *Chemistry and Industry*, 664 (1954): (b) S. Winstein and A. H. Fainberg, THIS JOURNAL, **78**, 2763 (1956).

TABLE I

EFFECTS OF LITHIUM PERCHLORATE ON IONIZATION OF I

Solvent	Temp., °C.	10^5k^0 sec.$^{-1}$	b	Av. fit % of k
AcOH[2b]	50.0	11.9	12.2[a]	0.6
50% AcOH–Ac_2O	50.0	6.43	13.1[b]	1.0
Me_2SO	75.0	18.2	0.0[c]	
$HCONMe_2$	75.0	4.96	1.4[c]	0.3
Ac_2O	75.0	3.41	47.1[b]	2.6
12.5% AcOH–Dioxane	75.1	1.22	462[d]	2.3
Me_2CO	75.1	0.857	47.0[c]	0.5
n-$C_7H_{15}COOH$	75.0	0.434	461[b,e]	1.6
EtOAc	75.0	0.113	553[b]	5.6
THF[f]	75.0	0.0847	482[c]	3.1
Et_2O	50.0	0.0006[g]	2.98[b,h] × 10^5	1.3

[a-d] ($LiClO_4$) range: [a] 0–0.06 *M*; [b] 0–0.10 *M*; [c] 0–0.05 *M*; [d] 0–0.07 *M*. [e] Equation 2; $c = 1184$. [f] Tetrahydrofuran. [g] 0.005 at 75°. [h] Equation 2; $c = 2.65 \times 10^6$.

competing ionization of the organic substrate and make it predominant.[3]

(3) S. Smith, J. Gall and D. Darwish, unpublished work.

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RECEIVED SEPTEMBER 21, 1959

RARE EARTH METAL–METAL HALIDE SYSTEMS. THE PREPARATION OF NEODYMIUM(II) HALIDES

Sir:

It has been suggested previously that the apparent solution of a number of metals in their molten halides is a result of the formation of a slightly stable, lower halide.[1] Although the subhalide is frequently stable only in dilute solution, in some systems the amount of reduction is sufficient to exceed the normal salt–lower salt eutectic composition so that the latter can be obtained as a stable solid.[2] These metal–metal halide studies are presently being extended to the rare earth systems, where knowledge of the reduction characteristics under these conditions has been limited to the Ce–$CeCl_3$ system. Here the reduction limit recently has been reported to be about 9 mole % Ce ($CeCl_{2.73}$) in a solution in equilibrium with liquid Ce and solid $CeCl_3$ at 777°,[3] in contrast to an earlier value of 32%.[4] Although evidence for an oxidation state lower than three for neodymium in aqueous solution has been doubtful,[5,6] and in liquid ammonia, inconclusive,[7] reduction of the molten trichloride and triiodide by metal has been found to yield the corresponding neodymium (II) halide. With praseodymium, reduction only in solution is observed with the chloride, while a new phase is obtained with the iodide.

The chlorides and iodides were prepared from the metals[8] and their reactions with metal studied in tantalum containers both by cooling curves and by analysis of salt phases in equilibrium with excess metal. The essentials of the phase diagram results are given in Table I. These salts were also equilibrated at higher temperatures with excess metal, quenched, and analyzed. For $PrCl_3$, X/M values for 6 runs at 978° averaged 2.34 ± 0.03; for $NdCl_3$, 6 at 950°, 2.00 ± 0.04; for NdI_3, 2 at 970°, 1.99 ± 0.05; incomplete separation of metal may make the X/M ratios somewhat low. Although phase equilibrium studies with PrI_3 are at present incomplete, powder patterns of the product from reaction with excess metal at >740° show a new phase and little PrI_3 to be present. The bronze product has an I/Pr ratio less than 2.6 and does not appear to be the diiodide.

TABLE I

	Eutectic		Reduction limit		
System	X/M	*T*, °C.	X/M	*T*, °C.	Solid phase
Pr–$PrCl_3$	2.50 ± 0.04	644 ± 5	2.50 ± 0.04	644 ± 5	Pr, $PrCl_3$
Nd–$NdCl_3$	2.56 ± .01	640 ± 3	2.01 ± 0.03	844 ± 2	$NdCl_2$
Nd–NdI_3	2.12 ± .02	492 ± 2	(2.0)	560 ± 5	NdI_2

The dark green $NdCl_2$ has been further identified from powder pattern data as isomorphous with the orthorhombic $PbCl_2$ structure reported for $SmCl_2$ and $EuCl_2$ by Döll and Klemm,[9] with lattice constants of 4.51, 7.58 and 9.07 A. ($SmCl_2$: 4.49, 7.53, 9.97 A.). Such a comparison has not yet been made for the dark purple NdI_2. Phase diagram and X-ray data for the $NdCl_3$–$NdCl_2$ system also show the existence of an intermediate phase near $NdCl_{2.3}$ in composition, melting probably incongruently near 703°.

Contribution No. 793. Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

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(1) J. D. Corbett, S. v. Winbush and F. C. Albers, THIS JOURNAL, **79**, 3020 (1957).

(2) J. D. Corbett and A. Hershaft, *ibid.*, **80**, 1530 (1958).

(3) G. Mellors and S. Senderoff, *J. Phys. Chem.*, **63**, 1110 (1959).

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(5) C. Estee and G. Glocker, *ibid.*, **70**, 1344 (1948).

(6) H. Laitinen and E. Blodgett, *ibid.*, **71**, 2260 (1949).

(7) P. S. Gentile, Ph.D. Thesis, University of Texas, Austin, Texas, 1955.

(8) We are indebted to Drs. F. H. Spedding and A. H. Daane for the generous supply of pure metal and the benefit of their experience in experimental techniques.

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RECEIVED AUGUST 7, 1959

CARBENOID AND CATIONOID DECOMPOSITION OF DIAZO HYDROCARBONS DERIVED FROM TOSYLHYDRAZONES

Sir:

Tosylhydrazones (*p*-toluenesulfonylhydrazones) of aromatic aldehydes and ketones react with sodium in ethylene glycol to give aryldiazoalkanes; tosylhydrazones of benzyl methyl ketone (equation 1) and cyclohexanone yield olefins and nitrogen.[1]

$$C_6H_5CH_2C(CH_3){=}NNHO_2SC_7H_7 + NaOCH_2CH_2OH \longrightarrow C_6H_5CH{=}CHCH_3 + N_2 + NaO_2SC_7H_7 + HOCH_2CH_2OH \quad (1)$$

Carbon-skeleton rearrangements occur in decomposition of pinacolone and camphor tosylhydrazones[1] to give 2,3-dimethyl-2-butene and camphene.[2]

An investigation has now been made of reactions of arylsulfonylhydrazones with bases in protonic and aprotic solvents. The experimental condi-

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(1) W. R. Bamford and T. S. Stevens, *J. Chem. Soc.*, 4735 (1952).

(2) See also R. Hirschmann, E. S. Snoddy, Jr., C. F. Hiskey and N. L. Wender, THIS JOURNAL, **76**, 4013 (1954) and G. H. Phillips, D. A. H. Taylor and L. J. Wyman, *J. Chem. Soc.*, 1739 (1954).