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(3) S. Smith, J. Gall and D. Darwish, unpublished work.

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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

System	Eutectic X/M	Eutectic T, °C.	Reduction limit X/M	Reduction limit T, °C.	Reduction limit 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).

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[4] D. Cubicciotti, THIS JOURNAL, **71**, 4119 (1949).

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

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[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.

[9] W. Döll and W. Klemm, *Z. anorg. allgem. Chem.*, **241**, 246 (1939).

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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).