

in the above calculations may reflect the differences of the spin states of cobalt(II) and cobalt(III) as well as the free energy of the elementary electron-transfer step.²² However, no such variation of oxidation potential seems sufficient to account for the discrepancy observed between values of k_{22} calculated for the V^{2+} and the $Ru(NH_3)_6^{2+}$ reactions. Marcus' theory is not invalidated by failing to account for the rates of reaction in a few particular cases. It does offer promise^{24,25} of correlating rates of electron transfer in a large number of "normal" cases, suggesting that some special effects are operating in the reactions of $Co(NH_3)_6^{3+}$ with reducing agents; one will need to go beyond the theory to discover what these special effects are.

In the reaction between $Co(NH_3)_6^{3+}$ and $Ru(NH_3)_6^{2+}$ the over-all free energy of activation should reflect some compromise between the standard oxidation potential

(22) This point has been discussed with regard to the standard oxidation potential of $Co(NH_3)_5OH_2^{2+} - Co(NH_3)_5OH_2^{3+}$.²³

(23) A. Haim and H. Taube, *J. Am. Chem. Soc.*, **85**, 499 (1963).

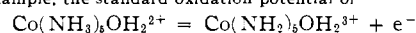
(24) G. Dulz and N. Sutin, *Inorg. Chem.*, **2**, 917 (1963).

(25) R. J. Campion, N. Purdie, and N. Sutin, *ibid.*, in press.

of $Co(NH_3)_6^{2+} - Co(NH_3)_6^{3+}$ and the standard oxidation potential (-1.8 v.¹³) of $Co(H_2O)_6^{2+} - Co(H_2O)_6^{3+}$ since the ultimate cobalt(II) product is $Co^{2+}(aq)$. Evidently the immediate cobalt(II) species, once formed, decays rapidly into the equilibrium cobalt(II) species. The other ruthenium(II)-cobalt(III) reactions reported in this paper seem to be more favorable thermodynamically.²⁶

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(26) For example, the standard oxidation potential of



has been estimated to be -0.33 v.²⁷

(27) R. G. Yalman, *Inorg. Chem.*, **1**, 16 (1962).

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The Role of Dissolved Lithium in the Reaction between Triethylsilane and Ethylamine

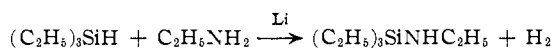
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The reaction of triethylsilane with ethylamine is not significantly catalyzed by dissolved lithium itself. Instead the reaction appears to be catalyzed by small amounts of a strong base such as lithium ethylamide, presumably present as an impurity in the lithium-ethylamine solution.

Introduction

In 1934 Kraus and Nelson¹ reported that triethylsilane reacts with ethylamine in the following way.



The stoichiometry with respect to Et_3SiH and H_2 was established, and the product Et_3SiNH_2 was isolated and identified. By adding the lithium to a solution of Et_3SiH in $EtNH_2$, they found that the reaction begins as soon as the blue color due to lithium develops, and (qualitatively) the rate of reaction increases as the Li concentration is increased. It was shown that an initial mole ratio of Li to Et_3SiH of either 1 or 0.1 results in catalysis. Accordingly, they concluded that "the reaction is a homogeneous one and the lithium evidently serves merely as a catalyst."

Later, in a paper devoted to preparative work utilizing this and similar reactions, Dolgov, *et al.*,² offered the view that the reaction is instead base-catalyzed, the base being the alkali amide formed by the reaction of the alkali metal with the solvent. Presumably the possibility of base catalysis was suggested in part by kinetic studies of the reaction between a trialkylsilane and alcohol or water, beginning with that of Price.³

Our main interest was in the possibility of genuine catalysis by lithium; if this were to take place, the reaction would offer a convenient means of studying the kinetics of a reaction involving a metal in solution.

Experimental

Reagents.—Anhydrous ethylamine (Eastman No. 506) was dried with metallic lithium and then distilled on the vacuum line into a storage vessel where it was kept over lithium wire until use. After each use, the ethylamine was distilled back to this storage vessel. For most experiments, triethylsilane (Peninsular ChemResearch No. 436) was sealed off in fragile Pyrex ampoules under vacuum. Triethylfluorosilane (Peninsular ChemResearch No. 2747) was redistilled. When used, it was outgassed on the vacuum line and condensed into the reaction flask. Small pieces of lithium metal (Lithium Corporation of America) were sealed off in fragile Pyrex ampoules under vacuum.

Apparatus and Procedure.—About 95% of the 420-ml. volume available to the reaction system consisted of a glass vessel which could be submerged in a thermostated bath in a dewar. The reaction vessel was connected to a manometer for pressure measurements. The solution and the gas above it were stirred with a multipole magnetic stirrer enclosed in an evacuated glass jacket and driven by a variable speed motor. Two evacuated glass tubes served as ampoule breakers. Each was sealed to a reagent ampoule (Li or Et_3SiH) and contained a small bar magnet allowing it to be manipulated by a horseshoe magnet outside the reaction vessel. The reaction vessel was thermostated in a strip-silvered dewar. The bath liquid (usually methanol) was periodically circulated through a cooling coil in a Dry Ice-methanol slush in a separate dewar by means of a self-priming pump, which was controlled by a thermistor temperature controller (Yellow Springs Instrument Co., Model 63RB). For most of the experiments, temperature stability was about $\pm 0.1^\circ$. Total drift in

(1) C. A. Kraus and W. K. Nelson, *J. Am. Chem. Soc.*, **56**, 195 (1934).

(2) B. N. Dolgov, N. P. Kharitonov, and M. G. Voronkov, *Zh. Obshch. Khim.*, **24**, 678 (1954).

(3) F. P. Price, *J. Am. Chem. Soc.*, **69**, 2600 (1947).

the course of several months of use was 0.2–0.3°. The temperature for the kinetic experiments was –31.5°.

The following procedure was followed in most of the experiments. If Et₃SiF was to be used, a known quantity was condensed into the reaction vessel. Ethylamine was distilled into the reaction vessel. A known weight of Li was subsequently added by breaking one of the ampoules. A known weight of Et₃SiH was added by breaking the other ampoule, thus starting the reaction. Pressure was measured as a function of time after Et₃SiH addition. After completion of the experiment, the ethylamine was distilled back to its storage vessel on the vacuum line.

Results

A set of experiments was done in which the concentrations of Li and Et₃SiH were varied, but no other reactant was deliberately added. If the reaction were catalyzed solely by Li and not at all by LiNH₂, this set of experiments should have established the rate law. In Table I, *t*_{1/2} (specifically the first half-life) is recorded for most of the experiments of this set. The wide scatter in the results is obvious. Pseudo-first-order kinetics (in Et₃SiH) were roughly followed during the major portion of most runs, though appreciable deviations were sometimes observed particularly in the early portion of the runs.

TABLE I
DIRECT KINETIC EXPERIMENTS

[Li] × 10 ² , M	[Et ₃ SiH] ₀ × 10 ² , M ^a	First <i>t</i> _{1/2} , min.
1.2	6.7	62
2.1	7.6	4
2.1	5.8	10
2.2	7.2	52
2.2	8.1	0.5
2.4	8.6	1.1
2.5	7.0	60
3.1	7.4	12
3.7	13.5	1.1
5.5	7.3	15

^a Subscript 0 indicates initial concentration.

Another set of experiments was done in which the procedure followed was essentially the same as in the ordinary kinetic experiments above, except that now some Et₃SiF was added to the EtNH₂ before adding Li and Et₃SiH. Two runs with Et₃SiF present which were not followed to completion of consumption of Et₃SiH are summarized in Table II. In expt. 17,

TABLE II
KINETIC EXPERIMENTS WITH Et₃SiF ADDED; NOT FOLLOWED TO COMPLETION

[Li] ₀ × 10 ² , M	2.7	2.4
[Et ₃ SiH] ₀ × 10 ² , M	8.0	9.7
[Et ₃ SiF] ₀ × 10 ² , M	19.0	0.59
Final % reaction ^a	0.0	1.3
Final <i>t</i> , min.	113	241
Experiment	17	18

^a Apparent per cent reaction when experiment was halted taken as final Δ*P*/calcd. Δ*P*_∞ × 100.

the blue color was observed to fade by *t* ≈ 65–72 min. (*t* is measured from the time of addition of Et₃SiH to the solution of EtNH₂, Li, and Et₃SiF).

Three experiments with Et₃SiF present which were followed to complete consumption of Et₃SiH are summarized in Table III. (There was some possibility of contamination in expt. 19.)

TABLE III
KINETIC EXPERIMENTS WITH Et₃SiF ADDED; FOLLOWED TO COMPLETION

[Li] ₀ × 10 ² , M	3.1	3.1	3.9
[Et ₃ SiH] ₀ × 10 ² , M	9.1	9.3	12.8
[Et ₃ SiF] ₀ × 10 ² , M	0.40	0.61	0.42
<i>t</i> at 5% reaction, ^a min.	194–216 ^b	266	121
<i>t</i> at 90% reaction, ^a min.	224	281	137
Experiment	19	20	21

^a Apparent per cent reaction, taken as Δ*P*_{*t*}/Δ*P*_∞ × 100.

^b Readings had not been taken during this interval.

For these same Et₃SiF experiments, Table IV summarizes data concerning the extent of H₂ production during the first 60 min. of reaction.

TABLE IV
DATA FOR *t* = 60 MIN. FOR THE EXPERIMENTS WITH Et₃SiF ADDED

[Et ₃ SiF] ₀ /[Li] ₀	7.1	0.25	0.13	0.20	0.11
Expected Δ <i>P</i> _∞ , cm.	23.3	26.2	23.6	22.8	27.8
Δ <i>P</i> _a if reaction of Li with EtNH ₂ were complete, cm.	3.9	3.2	4.0	3.8	4.2
Total Δ <i>P</i> _b at <i>t</i> = 60 min. (including increase before Et ₃ SiH addition), cm.	0.1	0.2	0.2	0.2	0.3
$\left[1 - \frac{2[\text{Et}_3\text{SiF}]_0}{[\text{Li}]_0} - \frac{\Delta P_b}{\Delta P_a}\right] [\text{Li}]_0^a \times 10^2, M$..	1.05	2.1	1.7	2.8
Experiment	17	18	19	20	21

^a Represents approximate lower limit for [Li] at *t* = 60 min. See text.

Discussion

It is apparent that the results of the direct kinetic experiments without Et₃SiF scatter widely (Table I). The conclusion to be drawn from these results is that although there may perhaps be a Li-catalyzed path available to the reaction, it is certainly not the only available path.

In principle, the question of the existence of a distinct Li-catalyzed reaction path in the case of a solution containing both Li and a strong base such as LiNH₂ could be resolved by observing the decrease in reaction rate brought about by removing either Li or LiNH₂ from solution without disturbing the other. As a practical matter, however, removing the LiNH₂ is likely to be preferable; since Li is ordinarily expected to be in large excess over LiNH₂, the amount of any reagent used to remove Li must also be large in comparison to the amount of LiNH₂ present, and the danger exists that low-level impurities in the reagent may consume significant amounts of LiNH₂. (In fact, before carrying out the Et₃SiF experiments, several experiments were done using Hg to try to determine the effect of extracting Li from the solution.

The rate was retarded in varying degrees, but since the Hg was present in very great excess over LiNH₂, these results presumably have little significance and will not be discussed further.)

In the series of experiments with Et₃SiF present, it was hoped that Et₃SiF might consume strong base impurities such as LiNH₂, while leaving most of the Li untouched. The basis for trying Et₃SiF was the observation by Gierut, *et al.*,⁴ that an attempted analysis of Et₃SiF for fluorine failed because Et₃SiF did not react with Na in liquid NH₃ at -33°. The first experiment of the Et₃SiF series (Table II) shows that Et₃SiF is not entirely unreactive toward Li in EtNH₂. However, even with 0.19 *M* Et₃SiF the 0.027 *M* Li was not consumed until about an hour after the Et₃SiH was added. Since the Et₃SiF concentrations used in the other Et₃SiF experiments (Tables II-IV) were only 2-4% as large as this, the direct reaction between Li and Et₃SiF should be relatively slow for the rest of the Et₃SiF series.

In all of the Et₃SiF experiments except the first, $0.11 \lesssim [\text{Et}_3\text{SiF}]_0/[\text{Li}]_0 \lesssim 0.25$. Thus Li is present in substantial excess over Et₃SiF. In Table IV is given an approximate lower limit for the Li concentration at *t* = 60 min. for the Et₃SiF series

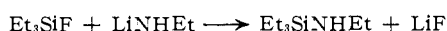
$$\left[1 - \frac{2[\text{Et}_3\text{SiF}]_0}{[\text{Li}]_0} - \frac{\Delta P_b}{\Delta P_a} \right] [\text{Li}]_0$$

This makes allowance for possible consumption of the Li. The actual Li concentration seems unlikely to be materially less than this value (with the possible exception of expt. 19) and may well be larger.

These lower limits are about the same size as Li concentrations in the ordinary kinetic experiments of Table I. Thus direct comparison of half-lives seems fair, projecting the initial rate observed up to *t* = 60 min. in expt. 18-21. The projected half-lives of more than 2000 min. in expt. 18-21 are more than 30 times as long as the longest half-life in Table I.

Thus the Et₃SiF experiments show that Li by itself does not significantly catalyze the reaction of Et₃SiH with EtNH₂.

Not only does the negligible rate in the early portion of these experiments show that Li does not significantly catalyze the reaction, but the rather abrupt onset of reaction at an accelerating rate after 2-4 hr. provides evidence that LiNH₂ or some similar strong base is a good catalyst for the reaction. A reasonable interpretation is the following: Li slowly reacts with EtNH₂ to give LiNH₂ and H₂. As long as Et₃SiF is present, this LiNH₂ apparently is rapidly consumed by the Et₃SiF, probably by means of the reaction



and thus cannot serve as a catalyst. However, as this reaction proceeds, Et₃SiF is slowly consumed. (It is probably somewhat more slowly consumed by direct reaction with Li.) When the Et₃SiF has been used up, the LiNH₂ starts to build up and can begin to catalyze the reaction. Thus the point at which the reaction takes place at an appreciable rate is taken to be the point at which Et₃SiF has been used up. (In

(4) J. A. Gierut, F. J. Sowa, and J. A. Nieuwland, *J. Am. Chem. Soc.*, **58**, 897 (1936).

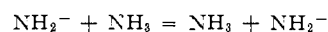
connection with Tables II and III, the H₂ pressure increase associated with complete consumption of Et₃SiF by LiNH₂ would correspond to an apparent per cent reaction of less than 5% in all cases except expt. 17.)

Although the above analysis suggests that a major catalyst is produced by reaction of Li with the solvent EtNH₂, identification of this catalyst as LiNH₂ is admittedly incomplete. For example, it is possible that after a short period of reaction, LiNH₂ might be converted to LiEt₃SiNH₂, if Et₃SiNH₂ is sufficiently more acidic than EtNH₂. This point was not pursued further since our primary interest was in whether or not the lithium was an effective catalyst. For simplicity, however, the base catalyst under discussion will be referred to as LiNH₂.

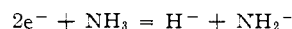
A very rough estimate can be made of the catalytic effectiveness of the base catalyst. In expt. 20, at *t* = 278 min., the specific rate constant corresponds to *t*_{1/2} = 2.4 min. Also, it appears that the pressure started increasing at an appreciable rate at about *t* = 265 min. If it is assumed that the rate of LiNH₂ production from 265 to 278 min. is approximately the same as during the first 265 min. of the reaction, judged by the pressure increase up to *t* = 265 min., then it appears that the *t*_{1/2} = 2.4 min. is due to a LiNH₂ concentration of about 4×10^{-4} *M*. Since in the experiments reported, [Li] was generally about $(2-5) \times 10^{-2}$ *M*, this indicates that a concentration of LiNH₂ only 1 or 2% as large as that of Li could, in these experiments, give a half-life of the order of 2-3 min. Small, irreproducible amounts of LiNH₂ would be a logical impurity in Li-EtNH₂ solutions.

Thus the active catalyst in the reaction between Et₃SiH and EtNH₂ is not Li, but apparently rather is a strongly basic impurity such as LiNH₂.

Recently there has been a revival of interest in a modification of the cavity model for metal-ammonia solutions, in the form of an ion-quadrupole model of the M₂ dimer.^{5,6} If such a picture applies also to solutions of lithium in ethylamine, it is interesting to note that the solvated electron pair appears to act as a substantially weaker base than LiNH₂ in the catalyzed Et₃SiH-EtNH₂ reaction and apparently also in the reaction with Et₃SiF. A similar comparison holds in at least one instance in metal-ammonia solutions, since the NH₃-NH₂⁻ exchange proceeds much more rapidly than the decomposition reaction of alkali metal-ammonia solutions.^{7,8} The reactions to be compared are



and



(H⁻ once formed would presumably rapidly form H₂).

Acknowledgments.—Fellowship support provided for A. V. by the National Science Foundation is gratefully acknowledged. This research was supported by the Atomic Energy Commission, Contract AT(11-1)-378.

(5) M. Gold, W. L. Jolly, and K. S. Pitzer, *ibid.*, **84**, 2264 (1962).

(6) M. Gold and W. L. Jolly, *Inorg. Chem.*, **1**, 818 (1962).

(7) R. A. Ogg, *Discussions Faraday Soc.*, **17**, 215 (1954).

(8) D. M. Yost and H. Russell, Jr., "Systematic Inorganic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1946, p. 137.