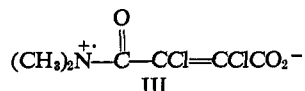
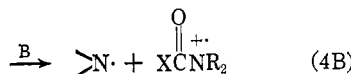
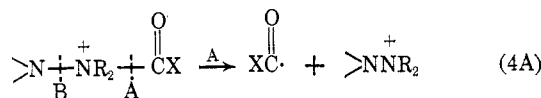
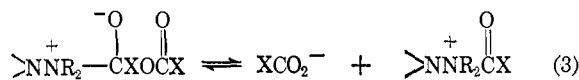


evolved vigorously at 0°, and a different esr spectrum (B) results (Figure 2). B gives splittings for one nitrogen ($a_N = 9.95$ gauss) and six equivalent hydrogens ($a_H = 10.66$ gauss). Spectrum B also is formed when glyoxal bisdimethylhydrazone or 1-phenyl-3,3-dimethyltriazene is treated with dichloromaleic anhydride, although acetic and maleic anhydrides do not result in observable radical formation. The spectrum is not caused by dimethyl nitroxide.⁵ From the observed splitting constants it is clear that there is extensive delocalization of spin from the nitrogen, and the g factor of 2.0046 ± 0.0002 shows that some spin density is on atoms heavier than nitrogen, for the g factor is determined mainly by the spin-orbit coupling constants of the atoms bearing spin density.⁶ We propose that the structure of B is III, which is consistent with extensive

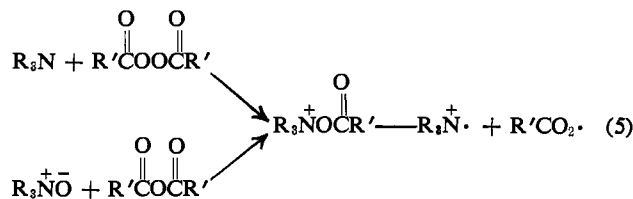


delocalization to a "transparent" group and the higher g factor of B than A, as well as being mechanistically reasonable. One might have predicted⁷ electron transfer from DMF, leading to the DMF cation radical. If exchange were rapid on the esr time scale, the hyperfine structure would collapse. Hyperfine structure is observed in DMF (line widths of *ca.* 350 mg were observed), so electron transfer from DMF to B must be slow. Experiments are in progress to assign the structure of B more firmly; we do not feel that lack of rapid electron transfer from DMF excludes III, which we favor for the structure of B.

The following mechanism is proposed for the radical-forming reactions ($R = \text{CH}_3$).



Equations 2 and 3 are not novel. Equation 4, the homolysis step, has analogy in the amine-induced diacyl peroxide decomposition, and the reaction of amine oxides with anhydrides thought to proceed through a common intermediate.⁸



(5) For which splittings $a_N = 16.1$, $a_H = 13.4$ gauss (G. Chapelet-Letourneux, *et al.*, *Bull. Soc. Chim. France*, **11**, 3283 (1965)) and $a_N = 15.2$, $a_H = 12.3$ gauss (J. Q. Adams, S. W. Nicksic, and J. R. Thomas, *J. Chem. Phys.*, **45**, 654 (1966)) have been reported.

(6) B. M. Trost and S. F. Nelsen, *J. Am. Chem. Soc.*, **88**, 2876 (1966).

(7) We wish to thank a referee for this suggestion.

(8) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p 590 ff.

In eq 4 a C-N⁺ (4A) or N-N⁺ (4B) homolysis replaces the O-N⁺ homolysis of eq 5. Whether bond A or B cleaves is determined by the stability of the radicals formed. The other radicals formed in steps 4A and 4B are not stable enough for convenient observation, but whereas no other absorptions besides those of II were observed with acetic anhydride and I, with phthalic anhydride other lines were obvious, though weak. Radical A (II) is observed at steady-state concentration in the anhydride reaction for, although the spectrum persists for several hours after mixing the components, the half-life of electrolytically generated II is about 2 min at room temperature. Maximum concentrations of A in the chemical generation are observed at about -20°. Below this temperature homolysis competes less effectively with radical decomposition. The behavior of spectrum B with temperature is similar. We have no evidence as yet on the relative timing of nitrogen loss and C-N homolysis in forming II from I.

Acknowledgment. Partial financial support of the above research by the Wisconsin Alumni Research Fund is gratefully acknowledged. We wish to thank Professor Evans for help with the electrolytic oxidation experiment.

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Received July 1, 1966

A Search for Hydrogen-Deuterium Exchange on Clean Aluminum Surfaces

Sir:

Aluminum films deposited at pressures in the neighborhood of 10^{-5} torr have given ample evidence of surface variability.¹⁻³ This variation, characterized by time-dependent changes in reflectance, is probably due to adsorption of oxygen and formation of coherent oxide layers. Aluminum deposited under high-vacuum conditions⁴ showed much more stability and has a higher initial reflectance in the infrared than do films deposited under low-vacuum conditions.

Trapnell's⁵ work and the work of Eley and Wilkinson⁶ indicate that aluminum *does not* chemisorb hydrogen, though some workers, Couper, Eley, Hulatt, and Rossington⁷ and Holden and Rossington,⁸ deduce some hydrogen chemisorption from data on ortho-para hydrogen conversion. Aluminum films deposited at 10^{-6} torr in an ambient air atmosphere should adsorb a monolayer of oxide in less than 10 sec, and the aluminum oxide thus formed may catalyze ortho-para conversion.⁹

A bakeable, ultrahigh vacuum system, routinely capable of pressures of the order 10^{-10} torr, was constructed

(1) G. Hass, W. R. Hunter, and R. Tousey, *J. Opt. Soc. Am.*, **46**, 1009 (1956).

(2) L. Holland, *Brit. J. Appl. Phys.*, **9**, 336 (1958).

(3) R. P. Madden, L. R. Canfield, and G. Hass, *J. Opt. Soc. Am.*, **53**, 620 (1963).

(4) H. E. Bennett, M. Silver, and E. J. Ashley, *ibid.*, **53**, 1089 (1963).

(5) B. M. W. Trapnell, *Proc. Roy. Soc. (London)*, **A218**, 566 (1953).

(6) D. D. Eley and P. R. Wilkinson, *ibid.*, **A254**, 327 (1959).

(7) A. Couper, D. D. Eley, M. J. Hulatt, and D. R. Rossington, *Bull. Soc. Chim. Belges*, **67**, 343 (1958).

(8) S. J. Holden and D. R. Rossington, *J. Phys. Chem.*, **68**, 1061 (1964).

(9) C. M. Cunningham and H. L. Johnston, *J. Am. Chem. Soc.*, **80**, 2382 (1958).

Table I. Analyses of Gas-Phase Composition Over 0° Films

Substrate	P, torr	Blank (HD), %	Exposed time, hr	% H ₂	% D ₂	% HD
Al ₁	150.3	0.3	10.2	68.9	30.2	0.9
Al ₂	357.7	0.5	11.5	50.0	48.5	1.5
Al ₃	390.9	0.5	14.8	36.7	61.4	1.9
Glass	357.6	0.7	9.98	59.1	39.1	1.8
Ni ₁	348.8	0.7	8.51	28.1	46.6	25.3
Ni ₂	367.0	0.7	9.34	32.0	17.9	50.1
Al + H ₂ O	150.7	0.7	10.2	49.4	47.8	2.8

and procedures for making clean aluminum films were developed. Aluminum of 99.999% purity was evaporated from rigorously pretreated, 20-mil tungsten helices. A very dense, smooth film of aluminum was evaporated onto 273°K substrate by heating the tungsten helix with 12 amp (ac) for 30 sec. During evaporation the pressure rose to values of $\sim 10^{-8}$ torr, but fell back to 10^{-9} torr within 30–60 sec. Electron microscopy of these films revealed them to be made up of relatively uniform crystallites of roughly hexagonal shape, about 0.5 μ in cross section with a few larger crystallites scattered throughout. These clean aluminum films were exposed to hydrogen and deuterium premixed behind a Granville–Phillips bakeable high-vacuum valve. The gases used in these experiments were obtained in 1-l. Pyrex flasks from the Air Reduction Co. The hydrogen was of 99.999% purity and the deuterium contained up to 2% H₂. For each experiment, a new mixing manifold was fused to the gas-handling system. Variation in the H₂/D₂ ratio is due to unequal flask and manifold volumes.

At the end of evaporation the pumps were isolated *via* another bakeable valve where the mixed gases were permitted to impinge on a freshly deposited film and the entire chamber permitted to communicate through a break-seal with a Wallace and Tiernan precision dial manometer.

A series of experiments in which the mixed H₂–D₂ pressures varied from 150.3 to 390.9 torr were conducted. In each case the substrate was maintained at 273°K. An identical filmless run was made, and similar runs were made with clean nickel films. At different intervals, gas-phase samples were taken and analyzed *via* low-temperature gas chromatography over 4-A molecular sieves. Another run was made in which the clean aluminum was first allowed to react with a small quantity of water vapor prior to treating with the premixed gases.

No evidence for chemisorption of hydrogen on clean aluminum at 273°K was forthcoming from these experiments. Within experimental limits, the baked glass substrate brought about as much H₂–D₂ conversion as did the aluminum films. Nickel films in the same experimental regime resulted in order of magnitude increases in conversion. The results of typical runs are shown in Table I.

An aluminum film exposed, prior to dosing with H₂ and D₂, to 2–3 mm of water vapor for several minutes gave increased conversion. The film was exposed to water vapor, which was then pumped out to forepump pressures ($\sim 10^{-4}$ torr). The system was closed off and only long-term exposure to mixed gases measured. For a blank of 0.7% HD, the exposure of this film to equimolar H₂ and D₂ for 10.2 hr at 150 torr resulted in conversion of 2.8%.

Clean aluminum exposed to large quantities of hydrogen at 273°K shows no evidence of chemisorption; however, if hydrogen chemisorption were an activated process, its absence at this temperature does not preclude chemisorption at higher temperatures. Data on chemisorption deduced from ortho–para^{7–8} changes are suspect because dissociative adsorption is not uniquely required for this process. Isotopic exchange, on the other hand, is a specific indication that dissociative chemisorption has taken place.

Our findings support those of Trapnell⁵ and others⁶ to the conclusion that aluminum does not chemisorb hydrogen, and it is believed that further systematic pursuit of this research will definitely assign the ortho–para conversion catalysis to contaminant films of aluminum oxide.

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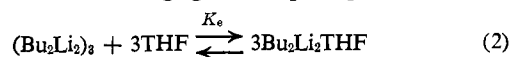
Solvent Effects in Organometallic Reactions. VI. A Kinetic Role of Base

Sir:

Application of eq 1 to analyze initial reaction rates, R_i , of organolithium reagents, RLi, with a number of different substrates, Z, in several basic solvents reveals that there is a common *kinetic role* for solvent, the second role of base in these reactions. The first,

$$R_i = k[\text{base}]^\alpha[\text{RLi}]^\beta[\text{Z}]^\gamma \quad (1)$$

a *thermodynamic role*,¹ is illustrated in eq 2; a base such as tetrahydrofuran, THF, reacts with an oligomer such as butyllithium hexamer, (Bu₂Li)₃,² to form a specific lithium dimer coordination complex, Bu₂Li₂THF. The fugacity of the base is slight in this complex; THF has negligible vapor pressure over



benzene solutions of BuLi if the base/lithium ratio, r , is less than 1/2.³ Because this thermodynamic role thus consumes some solvent, when r exceeds 1/2, the effective base, [base]_e, for the kinetic role is the difference between total base and half the total lithium; e.g., [THF]_e = [THF] – 1/2[BuLi]. Sub-

(1) G. W. Gibson and J. F. Eastham, *J. Am. Chem. Soc.*, **85**, 2171 (1963).

(2) D. Margerison and J. P. Newport, *Trans. Faraday Soc.*, **59**, 2058 (1963).

(3) For excellent kinetic data revealing the significance of an r value of 1/2 see Ye. A. Kovriezhnikh, V. M. Basmanova, and A. I. Shatenstein, *Org. Reactivity, Tartu State Univ.*, **1**, 103 (1964); A. I. Shatenstein, Ye. A. Kovriezhnikh, and V. M. Basmanova, *ibid.*, **2**, 135 (1965)