TABLE II

Investigated system	ΔE,[a] kcal./mole	Reference
$H_2 + CH_3 \rightarrow H + CH_4$ $D_2 + CH_3 \rightarrow D + CH_3D$	1.8	Photolysis,[b] 134–290°
$CH_3CO{\cdot}CH_3 + CH_3 \rightarrow CH_3CO{\cdot}CH_2 + CH_4$ $CD_3COCD_3 + CH_3 \rightarrow CD_3CO{\cdot}CD_2 + CH_3D$	1.64	Photolysis,[c] 150–250°
$CH_3{\cdot}CO{\cdot}CH_3 + CH_3 \rightarrow CH_3{\cdot}CO{\cdot}CH_2 + CH_4$ $CD_3CO{\cdot}CD_3 + CH_3 \rightarrow CD_3CO{\cdot}CD_2 + CH_3D$	1.67	Pyrolysis,[d] 466–525°
$CH_3{\cdot}CHO + CH_3 \rightarrow CH_3{\cdot}CO + CH_4$ $CH_3{\cdot}CDO + CH_3 \rightarrow CH_3CO + CH_3D$	1.1	Photolysis,[e] 27–165°

[a] It is assumed that CH_3 and CD_3 radicals react with the same activation energy. [b] E. Whittle and E. W. R. Steacie, *J. Chem. Phys.*, **21**, 993 (1953); see also J. R. McNesby, A. S. Gordon and S. R. Smith, THIS JOURNAL, **78**, 1287 (1956). [c] J. R. McNesby and A. S. Gordon, *ibid.*, **76**, 1416 (1954). [d] J. R. McNesby, T. W. Davis and A. S. Gordon, *ibid.*, **76**, 823 (1954). [e] P. Ausloos and E. W. R. Steacie, *Can. J. Chem.*, **33**, 31 (1955).

pounds and the best set of data is collected in Table II. It is necessary to state, however, that a few more systems were investigated, the results leading to ΔE's different from those quoted in Table II, *e.g.*, $CH_3 + CH{:}CH$ or $CD{:}CD$, $\Delta E = 4.4$ kcal./mole,[12] or $CH_3 + C_2H_6$ and C_2D_6 giving $\Delta E = 3.3$ kcal./mole.[13] It seems, however, that some unknown factors complicate these reactions and this vitiates the ΔE values. (In a letter to one of us Dr. Gordon expressed his doubts in the ΔE value obtained for the system C_2H_6–C_2D_6, although he is unable to spot any error in his experimental results.) Indeed, the work of Steacie and his school shows clearly the difficulty of accurate determination of ΔE, *e.g.*, their earlier results[14] obtained for the system

$$CH_3(CD_3) + H_2 \text{ and } CH_3(CD_3) + D_2$$

lead to ΔE values varying from 0.7 to 2.5 kcal./mole.

Our present results, as well as those quoted in Table II, show that ΔE is equal to the difference in the respective zero-point energies. For example, difference in zero-point energies of H_2 and D_2 amounts to 1.8 kcal./mole, and ΔE is also 1.8 kcal./mole, difference in C–H and C–D zero-point energies is 1.25 kcal./mole (from infrared spectra) the observed ΔE vary from 1.1 to 1.6 kcal./mole. This fact was recognized clearly by Bigeleisen[15]—it indicates the same configuration for the transition states in H and D abstractions and no zero-point energy in the transition state.

We prepared recently a sample of $C_6H_5CHDCH_3$ by reducing α-chloroethylbenzene with LiD + $LiAlD_4$ using the procedure described by Eliel.[16] Mass-spectroscopic analysis showed that the final product contained 96% of the required deuterated compound and 4% of ordinary ethylbenzene. Using this sample we determined ν_D/ν_H, *i.e.*, the ratio of the respective frequency factors of D or H abstraction reactions. The ratio CH_3D/CH_4 was determined at 132.3° using decomposition of di-*t*-butyl peroxide and at 49.1° using photolysis[1] of azomethane. On the basis of previously determined $\Delta E = E_D - E_H$, we obtained for ν_D/ν_H values 1.28 and 1.24, respectively. It is interesting to note that ν_D/ν_H determined by McNesby and Gordon for reactions $CH_3 + CH_3COCH_3$ and $CH_3 + CD_3COCD_3$ are 1.18 (ref. *c* of Table II) and 1.28 (ref. *d* of Table II). The agreement with our results seems to be well within experimental errors of these determinations.

While the present results were obtained in a liquid phase, those quoted in Table II arise from the work carried out in the gas phase. The agreement between these results indicates, therefore, that the course of a bimolecular free radicals reaction in a nonpolar solvent resembles closely that in the gas phase.

[12] C. H. Drew and A. S. Gordon, *J. Chem. Phys.*, **31**, 1417 (1959).

[13] J. R. McNesby and A. S. Gordon, THIS JOURNAL, **77**, 4719 (1955).

[14] T. G. Majury and E. W. R. Steacie, *Discussions Faraday Soc.*, **14**, 45 (1953).

[15] J. Bigeleisen, *J. Chem. Phys.*, **17**, 675 (1949).

[16] E. L. Eliel, THIS JOURNAL, **71**, 3970 (1947).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PITTSBURGH, PITTSBURGH 13, PENNSYLVANIA]

Lithium Aluminum Amides as Catalysts for the Reaction of Lithium Aluminum Hydride with 1-Hexyne[1]

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The rate of reaction of lithium aluminum hydride with 1-hexyne in ether has been studied. Catalysts for this reaction have been produced by the reaction of excess lithium aluminum hydride in ether on amines and related compounds.

By measuring the hydrogen evolved we have studied the rate of reaction of lithium aluminum hydride with 1-hexyne in ethyl ether at temperatures from 35 to 42°. The total hydrogen evolved is consistent with

$$LiAlH_4 + 4HC{\equiv}C{-}C_4H_9 \longrightarrow LiAl(C{\equiv}C{-}C_4H_9)_4 + 4H_2 \quad (1)$$

and there is no evidence of reduction of the triple bond, in agreement with results reported[2] for the reaction in dioxane. However, in a mixture of *n*-butyl ether and ethyl ether at 90°, less than the theoretical amount of hydrogen was evolved, and the infrared spectrum indicates that some alkyne was reduced to alkene.

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[1] This work was sponsored by the Office of Ordnance Research, U. S. Army.

[2] W. J. Bailey and C. R. Pfeifer, *J. Org. Chem.*, **20**, 1337 (1955).

Reaction 1 is slow in ethyl ether. At 42°, with the 1-hexyne initially one molar and a slight excess of lithium aluminum hydride, half of the total hydrogen was evolved in 500 minutes. Mathematical analysis of the rate data[3] showed that the kinetics deviates significantly from that of a mechanism involving consecutive second order steps, *viz.*

$$LiAlH_4 + HC{\equiv}C{-}C_4H_9 \longrightarrow LiAl(C{\equiv}C{-}C_4H_9)H_3 + H_2$$

$$LiAl(C{\equiv}C{-}C_4H_9)H_3 + HC{\equiv}C{-}C_4H_9 \longrightarrow LiAl(C{\equiv}C{-}C_4H_9)_2H_2 + H_2\text{, etc.}$$

This deviation is of such a nature that it might be explained if lithium aluminum hydride is associated in ether solution and if the degree of association is concentration dependent.[3] Ebullioscopic results which indicate that association of this type does take place in ethereal solutions of lithium aluminum hydride have been reported.[4] Also, vapor pressure studies currently underway in this Laboratory have given results which, though still incomplete, offer confirming evidence.

In an attempt to study the effects on the rate of reaction 1 of the presence of various bases, such as tertiary amines, it was discovered that catalysts can be produced by the reaction of lithium aluminum hydride on primary and secondary amines and related compounds. These results are described more fully in the following section.

Amines and Amine N-Oxides as Sources of Catalysts.—It was found that the presence of a small amount (less than 4% by volume) of triethylamine greatly increased the rate of reaction 1, and the rate became independent of the hexyne concentration. However, the effect of the amine varied greatly when samples of amine from different batches were used, even when the batches were obtained from the same stock bottle but distilled at different times. Results with the same batch of amine were reproducible. This indicated that most, or all, of the catalytic effect was caused by impurities in the triethylamine, which according to gas chromatographic analysis contained not more than 1% impurities.

Rather than attempting to identify the impurities in the triethylamine, we tested for catalytic effect several possible impurities and related substances. As a result of these tests it was discovered that catalysts can be produced by the reaction of excess lithium aluminum hydride in ether with substances (see Table I) such as ammonia, primary amines, secondary amines and amine N-oxides. Most of these substances react rapidly sometimes violently, with ethereal lithium aluminum hydride, and all except N-methylaniline and diphenylamine produce precipitates. Solutions of catalysts were made by treating about one gram of the amine, or related compound, with about 5 ml. of lithium aluminum hydride solution.

One ml. of the supernatant (or of homogeneous solution), when added to 35 ml. of an ether solution of 1-hexyne and lithium aluminum hydride, greatly increased the rate of reaction 1. From Table I a rough idea of the catalytic effects can be obtained. $t_{1/2}$ is the time required for half of the hexyne to react. Reference to this table is to be made with the understanding that the identities of the actual catalytic species and, therefore, their concentrations are unknown

TABLE I

Source of catalyst	Rate descrip., min.[a]
Ammonia[b]	$t_{1/2} = 90$
t-Butylamine	$t_{1/2} = 30$
Diethylamine	Instantaneous
Aniline	$t_{1/2} = 10$
N-Methylaniline	$t_{1/2} = 30$
Diphenylamine	$t_{1/2} = 70$
Piperidine	Instantaneous
Pyridine	$t_{1/2} = 10$
Pyridine N-oxide	$t_{1/2} = 4$
γ-Picoline N-oxide	4 (complete)
Triethylamine N-oxide	7 (complete)
No catalyst	$t_{1/2} = 500$

[a] The time required for half of the hexyne to react is indicated by $t_1/_2$. [b] In this case the catalyst was prepared by treating a 0.02 molar ethereal solution of ammonia with a lithium aluminum hydride solution. A 10 ml. portion of supernatant liquid from the resulting mixture was used as catalyst.

When treated with excess lithium aluminum hydride in ether the secondary and primary amines gave off one and two moles of hydrogen, respectively, per mole of amine, which is in agreement with results previously reported by other workers.[5,6] When precipitates are produced the products probably depend on the concentration of the reactants and on the manner of mixing. Because diphenylamine does not produce a precipitate when it is added to lithium aluminum hydride in ether, this amine was chosen for further study with the following results:

The catalyst produced by the diphenylamine is not nearly as effective as those produced by some of the other compounds, such as diethylamine and triethylamine N-oxide. The presence of these latter compounds could easily mask the effect of diphenylamine.

When excess diphenylamine was added to lithium aluminum hydride in ether, the system remained homogeneous, and the amount of hydrogen evolved indicated the product was $LiAlH_2(NPh_2)_2$. This product was about 100 times more reactive than lithium aluminum hydride toward 1-hexyne. When the hydride was in excess (1.5 moles of $LiAlH_4$ per mole of Ph_2NH), all of the remaining hydride was at least 100 times more reactive than untreated lithium aluminum hydride.

The rate of reaction 1 in the presence of moderate quantities of diphenylamine (for example, 0.1 mole/l.) is dependent upon the hexyne concentration, in contrast to the aforementioned effect of the impurities in triethylamine.

A solution containing lithium diphenylamide, prepared by reaction of lithium and phenyl bromide in ether followed by reaction with diphenylamine, had no effect on reaction 1.

The absence of catalysis by lithium diphenylamide in contrast to the effect of $LiAlH_2N(Ph_2)_2$

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(3) George B. Smith, Ph.D. Thesis, University of Pittsburgh, 1959.

(4) Norman G. Gaylord, "Reduction with Complex Hydrides," Interscience Publishers, Inc., New York, N. Y., 1956, p. 10.

(5) J. A. Krynitsky, J. E., Johnson and H. W. Carhart, THIS JOURNAL, **70**, 486 (1948).

(6) F. A. Hochstein, *ibid.*, **71**, 305 (1949).

suggests that bridge structures of the type $[H_2Al(NPh_2)_2AlH_4]^-$ may be reaction intermediates. The amide bridge has previously been postulated[7] in $(Me_2AlNMe_2)_2$

Reaction of Lithium Aluminum Hydride and Ethyl Bromide.—In an earlier study[8] the kinetics of the reactions of lithium aluminum hydride with *n*-butyl bromide and with *n*-amyl bromide in ether were investigated. In the present work the reaction of lithium aluminum hydride with ethyl bromide in ether was studied by following the rate of evolution of ethane. As in the cases of *n*-butyl and *n*-amyl bromides, the ethyl bromide-hydride system soon became heterogeneous. The evolution of gas became very slow after about one-fourth of the hydride had reacted. In order to test the effect upon this reaction of the catalysts for the hydride–hexyne reaction, some catalyst which had been prepared from pyridine N-oxide was added to the hydride-ethyl bromide system. No change in the rate or nature of the reaction was observed.

Experimental

1-Hexyne was prepared from sodium acetylide and freshly distilled *n*-butyl bromide in liquid ammonia. It was distilled twice and sealed in ampoules under dry nitrogen, b.p. 71°. **Ethyl bromide** (Dow Chemical Company) was dried over anhydrous magnesium sulfate and distilled. **Aniline**, *t*-**butylamine**, **diethylamine**, **N-methylaniline**, **piperidine** and **pyridine** were all dried over potassium hydroxide pellets and distilled. Samples of γ-**picoline** N-oxide, m.p. 180.5–181.2°, and **pyridine N-oxide**, which had been distilled at 80° and 1 mm. were obtained from Theodore Cohen, Department of Chemistry, University of Pittsburgh. The **diphenylamine** was Fisher Certified Reagent, m.p. 53.3–53.9°. The **triethylamine** was treated with lithium aluminum hydride in ether, distilled and sealed in ampoules under dry nitrogen.

The ether solution of lithium aluminum hydride was prepared by adding the pulverized solid hydride (Metal Hydrides, Inc.) to anhydrous ethyl ether and refluxing for eight hours. The resulting solution was filtered through a sintered glass filter under nitrogen pressure and standardized by measuring the hydrogen evolved upon the addition of excess alcohol. Also, a weighed sample of the solution was placed on a vacuum line and the ether was completely removed and measured. The weight of solids agreed with standardization results when the empirical formula was assumed to be $LiAlH_4$.

The apparatus and method for the rate measurements were essentially those which were used previously[9] for kinetic studies of some Grignard reactions. The reactions were followed by measuring the volume of a gaseous product. The solvent vapor was removed from the gaseous product and returned to the reacting mixture by a cold finger type Dry Ice–acetone condenser. The reacting mixture was maintained in a refluxing condition, and the reaction temperature was controlled by regulating the pressure. Duplicate runs gave results (volume *vs.* time) which agreed within 1% under the most favorable conditions. For rapid reactions, such as those with a half-life of less than ten minutes, the precision was not that good.[3]

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[7] N. Davidson and H. C. Brown, THIS JOURNAL, **64**, 316 (1942).

[8] D. J. Walter, John H. Wotiz and C. A. Hollingsworth, *ibid.*, **78**, 1311 (1956).

[9] John H. Wotiz, C. A. Hollingsworth and Raymond E. Dessy, *J. Org. Chem.*, **19**, 1545 (1955).

[CONTRIBUTION FROM THE IPATIEFF HIGH PRESSURE AND CATALYTIC LABORATORY, DEPARTMENT OF CHEMISTRY, NORTHWESTERN UNIVERSITY, EVANSTON, ILLINOIS]

Alumina: Catalyst and Support. IV.[1] Aromatization and Dehydroisomerization of 1,1-Dimethylcyclohexane, 4,4-Dimethylcyclohexene and of Methylcycloheptane over Chromia-Alumina Catalysts[2]

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The aromatization of 1,1-dimethylcyclohexane (I), 4,4-dimethylcyclohexene (II) and of methylcycloheptane over chromia alone and chromia–alumina catalysts having different intrinsic acidities was studied. It was found that chromia alone is a dual function catalyst, it has both dehydrogenation and isomerization properties. In the presence of this catalyst compounds I and II on aromatization yield toluene and xylenes. Chromia–alumina catalyst prepared from alumina having intrinsic acidity aromatized compounds I and II to a mixture of hydrocarbons consisting of toluene, xylenes and ethylbenzene. When a catalyst prepared from alumina of low intrinsic acidity was used, only toluene was produced. The effect of the various catalysts upon the aromatization of methylcycloheptane has been studied. The dehydroisomerization reaction is nterpreted as deriving from the acidic character of the catalyst.

Introduction

The use of chromia–alumina as a catalyst for the dehydrogenation and aromatization of hydrocarbons has been studied extensively. In none of the published papers, however, is it suggested that alumina may exert an effect upon the catalytic properties of the mixed catalyst and that the products resulting from such aromatization reaction may depend to a great extent upon the type of alumina.

Recent studies in our Laboratory have revealed that alumina has intrinsic acidic properties and that the strength of the acid sites depends upon the method used for the preparation of the aluminas.[4] It also has been shown recently that the change in the C^{14} distribution pattern during the aromatization reaction of *n*-heptane-1-C^{14} and *n*-octane-1-C^{14} depends upon the type of alumina used in the preparation of the chromia–alumina catalysts.[5] It was also observed that the differing types of alumina influence the catalytic behavior of molybdena–alumina catalysts.[6]

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[1] For paper III of this series see W. O. Haag and H. Pines, THIS JOURNAL, **82**, 2488 (1960). Paper II of the series "Aromatization of Hydrocarbons." For paper I see ref. 5.

[2] This research was supported by a grant from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of said Fund.

[3] (a) For a review of the literature see: A. H. Steiner, in "Catalysis," Vol. IV, edited by P. H. Emmett, Reinhold Publishing Corporation, New York, N. Y., 1956, pp. 529–560. (b) G. F. Ciapetta, R. M. Dobres and R. W. Baker, *ibid.*, pp. 492–692.

[4] H. Pines and W. O. Haag, THIS JOURNAL, **82**, 2471 (1960).

[5] C. T. Chen, W. O. Haag and H. Pines, *Chem. & Ind.* (*London*), 1379 (1959).

[6] H. Pines and G. Benoy, THIS JOURNAL, **82**, 2483 (1960).