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Studies on the Catalytic Reduction of Acetone[1]

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Catalytic reductions of acetone to propane and isopropyl alcohol have been investigated using deuterium. A mechanism involving direct addition of deuterium is favored in both reactions. The synthesis of $(CH_3)_2CD_2$ by this method is not possible because of exchange of deuterium with an intermediate in the reduction process. Conditions have been found for the synthesis of $(CH_3)_2CDOD$.

Introduction

The catalytic reduction of acetone by deuterium was investigated with two objectives in view; the first was to develop methods of localized introduction of tracer deuterium into organic molecules and the second was to study the mechanism of the reduction process.

Farkas and Farkas[1a] and Anderson and MacNaughton[1b] had previously studied this reduction but the former workers limited their investigation to analysis of the deuterium content of the unconverted hydrogen and pressure measurements on the reacting system while the latter used a relatively low deuterium concentration and Raman spectra for analysis of their products.

Kauder and Taylor[2] have recently published the results of a study which was carried out simultaneously with and closely parallel to the research reported in this paper. The basic method of reduction with deuterium and analysis of the products for number and distribution of deuterium atoms was the same. The similarity in the results of the catalytic reduction of acetone on different catalyst preparations is remarkable. However our experiments were directed more along the lines of obtaining conditions of localized introduction of deuterium in the molecule by going to lower temperatures and shorter contact times rather than making a detailed examination of the kinetics of the exchange of propane and deuterium of the type reported by Kauder and Taylor. Furthermore, in spite of the failure to obtain the localized introduction of tracer deuterium into propane, some experiments in which acetone was converted to isopropyl alcohol are reported in which some degree of success was obtained in the localized introduction of deuterium into this molecule.

Experimental

The apparatus for the gas phase reduction and exchange studies was a flow system in parallel with a sylphon bellows circulating pump. The catalyst chamber, containing 1 g. of Baker and Co. 10% platinum-on-charcoal, was heated to a temperature of 120° for a period of 12 hours under vacuum, cooled to room temperature and flushed twice with small batches of D_2 to displace any adsorbed H_2. In a typical run a mixture of two parts D_2 to one part of acetone at a total pressure of 150 mm. was admitted to the catalyst chamber. The gas was recycled through the platinum charcoal by means of the sylphon pump for five minutes. The mixture was then pumped out through a trap which was cooled with liquid nitrogen. The product propane was then separated from the unreacted acetone by distilling the propane into an evacuated sample tube cooled in liquid nitrogen from a trap cooled with Dry Ice. The product was then analyzed with a Consolidated-Nier type mass spectrometer. In a similar manner the exchange of propane with D_2 and of isopropyl alcohol with D_2 was studied. The behavior of propane-2-*d* on platinum-on-charcoal was also investigated in this system.

Experiments were carried out in which a mixture of D_2 and acetone was pumped through the catalyst chamber and trap. The flow rate was estimated at 30 cc./min. The condensable products were trapped, fractionated and analyzed in the manner described above. Finally, a run was made in which pure acetone was pumped through the catalyst bed; the system was then evacuated to one micron, D_2 was flushed through the catalyst and the condensable gases trapped and analyzed.

Experiments were carried out on the reduction of liquid acetone in a Parr hydrogenation apparatus and an Aminco Superpressure hydrogenation unit at room temperature. The catalysts used here were iron promoted platinum-on-charcoal and Adams platinum catalyst.[3] In the pressure reductions, tank deuterium was used at pressure ranging from 350–450 pounds. The products of reduction carried to completion were analyzed directly in the mass spectrometer. The products of the runs in which only a small fraction of the acetone was reduced were distilled in a 45-cm. vacuum jacketed Vigreux column before analysis.

Analytical

Partial mass spectra of propane, isopropyl alcohol and acetone which were used as a basis of analysis are presented in Table I. Electron bombardment of propane in the mass spectrometer results in the ionization of the molecule to produce $C_3H_8^+$ and also lower mass ion fragments by rupture of C–H and C–C bonds. If propane-2-*d*-2 were formed in the deuterium reduction of acetone by addition of D_2 to the carbonyl linkage the most abundant C_3 ion would be the parent ion $C_3H_6D_2^+$. In the C_2 group, since both methyls would contain only protium, the most abundant ion would be $CH_3CD_2^+$ at mass 31. The C_1-group would contain no ions above mass 15 (CH_3^+), providing no rearrangement took place. In the event that an exchange reaction accompanied the reduction process a distribution of masses could be obtained up to mass 52, ($C_3D_8^+$). Such a complex mass spectrum can be analyzed in the following way: the ion currents corresponding to masses 52 and 51 directly indicate the amounts of C_3D_8 and C_3D_7H in the mixture provided that suitable C^{13} corrections have been made. Ions of mass 50 and lower are formed by ionization of the $C_3D_6H_2$ molecule and also by dissociation of higher molecular weight polydeuteropropanes. The near equality of the appearance potentials of $C_3H_7^+$ and $C_3H_8^+$ make it impossible to determine the latter in the absence of the former by working at electron accelerating voltage below the appearance potential of $C_3H_7^+$.[4] The mass spectra of the individual polydeuteropropanes are required to determine the relative abundance of the dissociation products and indirectly the abundance of the molecular ions of lower mass in the complex mass spectrum. Unfortunately, these patterns are not available but an approximation may be made by assuming that the probability of rupture of C–H and C–D bonds by electron impact is identical and that the mass spectra of the polydeuteropropanes may be calculated from that of propane with purely statistical rupture of C–H and C–D bonds. This approximation is probably very good for C_3D_8 but its limitations in the case of partially deuterated hydrocarbons

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(1) (a) A. Farkas and L. Farkas, THIS JOURNAL, **61**, 1336 (1939); (b) L. C. Anderson and N. W. MacNaughton, *ibid.*, **64**, 1456 (1942).

[2] L. N. Kauder and T. I. Taylor, *Science*, **113**, 240 (1951).

[3] "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941.

[4] D. P. Stevenson and C. D. Wagner, THIS JOURNAL, **72**, 5612 (1950).

become obvious upon examination of the mass spectra of the monodeutero hydrocarbons.[5]

TABLE I

ION INTENSITY

Mass	Propane	Acetone	Isopropyl alcohol
60		0.1	0.5
59		1.3	3.5
58		33.1	0.2
57		0.4	0.5
46			2.3
45	3.3		100.0
44	100.0	2.4	3.7
43	82.4	100.0	18.3
42	21.0	6.8	4.3
41	43.4	1.9	7.3
40	8.7	0.7	1.0
39	55.7	3.4	

The mass spectrum of isopropyl alcohol is sufficiently different from that of acetone so that isopropyl alcohol and acetone may be readily determined in the presence of each other. Since the abundance of the molecular ion in isopropyl alcohol is rather low the number of D atoms per molecule is estimated from the ions of mass 45 and above. CH_3CHOH^+ at 45 is formed by the loss of a methyl group and equal probability of splitting off either of the two methyl groups is assumed. Thus the observed exchange estimated from the intensity of the ions at mass 45 and above may be low by a factor of two. A more detailed discussion of the mass spectrum of D substituted isopropyl alcohols is presented in another publication.[6]

Results

The relative intensities of the C_3-ions produced by electron bombardment of the products of the various gas phase reduction are presented in Table II. The corresponding distributions of polydeuteropropanes calculated by the method described in the analytical section are given in Table III. It is obvious from the data presented that in all the experiments performed, the reduction process is accompanied by an exchange reaction producing polydeuteropropanes up to and including C_3D_8.

Experiments were carried out to determine whether the exchange reaction involved the product propane or the reactant acetone. No exchange was observed between propane and deuterium after five minutes of recycling a 1:1 mixture at 25° over the reduction catalyst. A relatively slow exchange was observed with unreacted acetone under the conditions of the reduction. Approximately 5% of one C–H bond was converted to C–D and no molecules containing 2 C–D bonds were observed.

Isopropyl alcohol was found to be slowly converted to propane on this catalyst. The unreacted material showed exchange of only one hydrogen atom at room temperature, probably on the O–H bond.

The possibility of a series of intermolecular hydrogen exchanges among deuteropropanes was investigated by recycling propane-2-*d* for one hour over the catalyst at 25°. No change in the propane-2-*d* mass spectrum was observed after such treatment.

TABLE II

ION INTENSITY

I, Reduction in a flow system at −77°; II, reduction in a static system, recycled at 25° for five minutes; III, reduction in a static system, recycled at 0° for five minutes; IV, repeat of III; V, reduction in a static system, 10 hours contact time at 25°; VI, reduction carried out by flushing adsorbed acetone on the catalyst with deuterium.

Mass	I	II	III	IV	V	VI
52	0.8	0.5	3.0	1.0	0.09	3.2
51	1.6	1.7	6.0	2.5	.36	4.8
50	3.0	4.6	10.0	4.0	.92	8.5
49	4.7	9.1	13.3	6.0	1.69	10.0
48	6.5	15.0	15.9	8.6	2.53	12.1
47	8.8	21.5	18.6	12.5	3.54	14.0
46	16.8	28.5	30.0	24.5	5.37	19.5
45	13.2	28.5	24.5	23.5	7.14	16.2
44	12.7	25.8	22.0	22.5	8.51	15.9
43	9.0	16.0	27.7	20.5	4.91	10.5

TABLE III

DISTRIBUTION OF POLYDEUTEROPROPANES

I, Reduction in a flow system at −77°; II, reduction in a static system, recycled at 25° for five minutes; III, reduction in a static system, recycled at 0° for five minutes; IV, repeat of III; V, reduction in a static system, 10 hours contact time at 25°; VI, reduction carried out by flushing adsorbed acetone on the catalyst with deuterium.

	I	II	III	IV	V	VI
C_3D_8	2.4	0.8	4.4	1.8	0.6	7.3
C_3D_7H	4.8	2.6	8.8	4.6	2.3	10.9
$C_3D_6H_2$	6.3	6.0	9.8	6.9	5.2	11.8
$C_3D_5H_3$	8.6	10.2	9.4	5.3	8.0	10.5
$C_3D_4H_4$	11.9	15.6	12.5	9.2	10.2	14.8
$C_3H_5D_3$	15.5	19.8	14.8	15.0	13.0	17.8
$C_3H_6D_2$	32.8	23.2	25.6	29.6	20.2	20.3
C_3H_7D	7.8	15.3	6.2	14.5	22.0	8.4
C_3H_8	9.9	9.7	8.4	13.4	18.9	8.9

The reduction of acetone in the liquid phase in a Parr Hydrogenation unit using an unpromoted Adams Pt catalyst yielded only a small amount of polydeuteropropane.

Reduction of acetone to isopropyl alcohol went quite smoothly at 2 atmospheres pressure and room temperature on iron promoted platinum-on-charcoal. Batches consisting of one-half gram of catalyst and 20 cc. of acetone were treated. Mass spectra of the products obtained by partial and virtually complete reduction of acetone are presented in Table IV. In both cases some of the O–D deuterium was replaced by O–H by exchange in the mass spectrometer. Examination of the 48, 47 and 46 peaks shows that in addition to reduction there is a small amount of exchange. Slightly more than 2 atoms are introduced into the reduction product but this is minimized by stopping the reduction after a small fraction of the acetone has been converted. Exchange of the reduction product with light water removed a D atom from the molecule, the O–D. The 46 ion mass was then assigned a relative intensity of 100, while the 47 dropped to 5.3 and the 45 to 22.3 units of relative ion intensity. The 47 peak intensity arises in part from D exchange in the reduction process and C^{13} in the isopropyl alcohol. These results show that the predominant product of the reduction is $(CH_3)_2CDOD$.

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[5] J. Turkevich, L. Friedman, E. Solomon and F. Wrightson, *ibid.*, **70**, 2638 (1948).

[6] L. Friedman and J. Turkevich, *ibid.*, **74**, 1666 (1952).

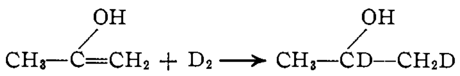
TABLE IV

RELATIVE ION INTENSITY

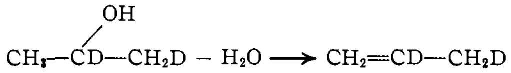
Mass	98% of acetone reduced	16% of acetone reduced
64	0.02	0.06
63	.12	.08
62	.49	.39
61	.92	.83
60	3.25	2.92
59	2.88	3.46
58	2.89	1.72
49	0.64	0.26
48	8.5	3.90
47	100.0	100.0
46	81.0	121.0
45	19.1	24.2
44	14.9	18.2
43	20.5	18.2
42	9.6	11.4
41	5.75	6.4
33	0.9	0.6
32	3.8	2.9
31	2.7	2.2
30	5.0	4.4
29	7.65	5.9
28	16.0	18.5
27	10.4	9.1

Discussion of Results

Two mechanisms have been proposed for the reduction of carbonyl compounds, reduction of an enol and direct addition of hydrogen across the C–O double bond. In the gas phase reduction to propane, Farkas and Farkas[1a] eliminated the enolic mechanism on the grounds that isopropyl alcohol would be an intermediate in the process and that isopropyl alcohol was reduced more slowly to propane than acetone. Furthermore, an enolic mechanism would involve exchange and they observed no exchange at low temperatures. An enolic mechanism with no accompanying exchange would permit the introduction of four D atoms per molecule of propane as



$$CH_3-\overset{OH}{C}=CH_2 + D_2 \longrightarrow CH_3-\overset{OH}{C}D-CH_2D$$



$$CH_3-\overset{OH}{C}D-CH_2D - H_2O \longrightarrow CH_2=CD-CH_2D$$

$$CH_2=CD-CH_2D + D_2 \longrightarrow CH_2D-CD-CH_2D$$

It is interesting to note that the peak of the distribution of the polydeuteropropanes is found at 46 or $C_3H_6D_2$. This would confirm Farkas and Farkas'[1a] hypothesis that reduction took place *via* direct addition of D_2 to the double bond. The fact that they observed no exchange may be ascribed to relatively insensitive method of detection, *i.e.*, analysis of unreacted D_2. Even direct analysis of the reduction product for D_2 by combustion would be relatively insensitive, yielding an average of 2.3–3.5 atoms of D per molecule of propane on runs I–IV. In run VI, where the ratio of D_2 to acetone was high, the average D content is slightly higher, 4.2 atoms per molecule.

The results show exchange taking place at temperatures as low as −77°. The fact that the exchange is more rapid than any occurring with either the reactant or product leads to the conclusion that it takes place with an activated complex undergoing reduction and nullifies any attempt at localized introduction of D by this method into propane.

Anderson and MacNaughton[1] report direct addition of D_2 in the reduction of acetone to isopropyl alcohol at room temperature and an enolic exchange mechanism at higher temperatures. Apparently the relative rates of exchange and reduction carried out in the liquid phase are such that a separation of these processes may be made. Exchange reactions in liquids may be minimized in two ways: (a) by a larger concentration of hydrogen acceptor molecules competing for activated hydrogen and thus reducing the amount available for exchange, and (b) by having a large excess of substrate serve as a solvent for the reduction product facilitating rapid removal of the products of reduction from the catalyst surface. The latter ideas are somewhat speculative since the presence or absence of exchange may be purely a function of the catalyst, but they serve to suggest lines of attack to the problem of localized introduction of D_2 into molecules by catalytic reduction.

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