

[CONTRIBUTION NO. 132 FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF TENNESSEE]

The Effects of Certain Nitro and Related Compounds upon the Rate of Exchange of Deuterium Gas with Acetic Acid over Adams Platinum Catalyst

BY HILTON A. SMITH AND EDGAR L. MCDANIEL

RECEIVED JULY 26, 1954

The effect of a nitro compound upon the rate of catalytic exchange of deuterium and acetic acid is determined by the remainder of the molecule. Where the nitro group is conjugated with an olefinic bond, the rate of exchange is accelerated by the addition of these compounds in low concentration. In more concentrated solutions of these compounds no exchange occurs initially, although exchange does occur after reduction of the nitro compound. Oximes derived by partial reduction of the nitro compounds in which the nitro group is conjugated with an olefinic bond increase the rate of exchange to values near those maxima exhibited by the parent nitro compounds.

Previous work¹ on the exchange between deuterium gas and acetic acid over Adams platinum catalyst has been extended. Line, Wyatt and Smith¹ found that this exchange was first order with respect to deuterium pressure and essentially zero order with respect to acetic acid. The rate of exchange was also proportional to the quantity of catalyst present. It was found that small amounts of nitrobenzene in the acetic acid completely prevented the exchange while nitroethane had no appreciable effect. These results were explained with the aid of catalytic hydrogenation data² on these compounds.

Since additional nitro compounds had been hydrogenated over Adams platinum catalyst in acetic acid and their kinetics elucidated,² it was desired to study the effect of these compounds on the deuterium-acetic acid exchange. When this was done the interesting behavior of some of these nitro compounds led to the syntheses of certain oximes and the study of their effect upon the exchange. These oximes were shown by Smith and Bedoit³ to be formed as a result of the catalytic hydrogenation of the nitro compounds.

Experimental

Materials.—Du Pont C.P. glacial acetic acid and J. T. Baker Chemical Company purified grade aniline were purified as in previous work.² Adams platinum catalyst was prepared in the usual manner.³ 2-Nitro-1-butene was synthesized by the method of Smith and Bedoit.³ The product was purified by distillation *in vacuo* through a 30-cm. Vigreux column; b.p. 30–32° (6 mm.), n_D^{25} 1.4358 (reported 39.5° (15 mm.), n_D^{25} 1.4358).² Nitromesitylene was prepared by the nitration of mesitylene.⁴ The crude product was treated with activated charcoal and then recrystallized three times from absolute ethanol. The final product melted at 43.2–44.3° (reported 43–44°).⁴ β -Nitrostyrene was prepared as directed in *Organic Syntheses*.⁵ The crude product was treated with activated charcoal and recrystallized three times from absolute ethanol; it melted at 56.8–57.5° (reported 57–58°).⁵

Methyl ethyl ketoxime was prepared by treating methyl ethyl ketone with hydroxylamine.⁶ The crude oxime was purified by fractional distillation through a 4-foot Vigreux column; b.p. 148.4° (741 mm.), n_D^{20} 1.4414 (reported b.p.

152–155° (cor.), n_D^{20} (1.4428).^{7,8} Phenylacetaldoxime was prepared⁹ by treating phenylacetaldehyde which had been purified by means of bisulfite addition compound, with hydroxylamine. The crude oxime was recrystallized three times from 33% ethanol to yield a white crystalline material, m.p. 96.5–98.0° (reported 97–99°).¹⁰ Deuterium gas was obtained from the Stuart Oxygen Company.

Exchange Apparatus and Procedure.—The exchange apparatus and procedure were essentially those described in previous work.¹ Six milligrams of Adams platinum catalyst was used in each exchange. The compounds studied were dissolved in pure acetic acid to give a total volume of 10 ml. All exchanges were carried out at 35 ± 0.2°, the reaction time being three minutes unless otherwise stated.

Analyses.—The analytical apparatus was essentially that described earlier.¹ The manifold was modified by the elimination of all rubber connections and by thermostating the effusion chamber. The void in the hole through the barrel in the two-way stopcock leading to the pinhole was minimized by use of a Kel-F (fluorocarbon) insert which reduced the effective bore to 0.25 square millimeter. All effusions were carried out at 35 ± 0.2°. Calculations were made as in earlier work.¹ Percentage exchange is defined as the atomic per cent. hydrogen in the gas phase.

Data and Results

All exchange values are the average of at least three separate determinations unless otherwise specified.

Deuterium gas exhibited a 28.5% exchange with pure acetic acid under the conditions of these experiments (Table I). Benzene at a concentration of 1.125 moles per liter reduced the exchange of acetic acid and deuterium to 11.5%. Since Line, *et al.*,¹ had found that the addition of nitrobenzene to acetic acid completely prevents the exchange reaction in solutions of moderate concentrations, the effect of aniline, a reduction product of nitrobenzene, on the exchange was studied. It is seen (Table I) that aniline in low concentrations reduced the amount of exchange, but a concentration was soon reached where the addition of more aniline failed to affect further the exchange. Similar behavior was noted in the case of nitromesitylene. β -Nitrostyrene and 2-nitro-1-butene each increased the rate of exchange in low concentrations, but as the concentrations were increased this effect passed through a maximum and in solutions of higher concentrations no exchange was detected for these systems within the three minute reaction time. There was an intense green color imparted to these nitro olefin systems during the exchange.

(7) A. Janny, *Ber.*, **15**, 2779 (1882).(8) C. Trapesonazjanz, *ibid.*, **26**, 1433 (1893).

(9) A. I. Vogel, "A Textbook of Practical Organic Chemistry," Longmans, Green and Co., New York, N. Y., 1948, p. 685.

(10) W. Dollfus, *Ber.*, **25**, 1917 (1892).(1) L. E. Line, Jr., B. Wyatt and H. A. Smith, *THIS JOURNAL*, **74**, 1808 (1952).(2) H. A. Smith and W. C. Bedoit, *J. Phys. Colloid Chem.*, **55**, 1085 (1951).(3) R. Adams, V. Voorhees and R. L. Shriner, *Org. Syntheses*, **8**, 92 (1928).(4) G. Powell and F. R. Johnson, *ibid.*, **14**, 68 (1934).(5) D. E. Worrall, *ibid.*, **9**, 66 (1929).

(6) R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," 3rd ed., John Wiley and Sons, Inc., New York, N. Y., 1948, p. 202.

TABLE I

THE EXCHANGE OF DEUTERIUM GAS OVER ADAMS PLATINUM CATALYST WITH CERTAIN ACETIC ACID SOLUTIONS

Solute	Concn., moles/l.	Exchange, %
None (pure acetic acid)		28.5
Benzene	1.125	11.0
Aniline	0.0025	23.4
	.01	21.0
	.10	21.2
Nitromesitylene	.001	27.8
	.01	25.9 ^a
	.10	23.0 ^a
	1.0	23.2 ^a
<i>β</i> -Nitrostyrene	.001	30.2
	.005	44.6
	.01	45.7
	.05	17.8 ^b
	.10	2.2 ^b
	1.0	0 ^b
2-Nitro-1-butene	0.010	39.7
	.051	47.8
	.077	8.3 ^c
	.102	0 ^d
	1.02	0 ^d

^a These solutions were pale yellow after the exchange.

^b These solutions were a brilliant chartreuse in color after exchange. ^c Pale amber solutions after exchange. ^d Green-brown solutions after exchange.

This interesting behavior suggested the study of certain oximes shown by Smith and Bedoit² to be formed by the catalytic hydrogenation of *β*-nitrostyrene and 2-nitro-1-butene. It was found that each oxime increased the rate of exchange initially (see Table II), eventually reaching the point where the addition of more oxime failed to change further the rate of exchange. In neither case did the rate of exchange with the oximes present in relatively high concentration fall below that exhibited by pure acetic acid. However, the highest level reached was not as great as the maximum exhibited in the case of each of the parent nitro compounds.

TABLE II

THE EXCHANGE OF DEUTERIUM GAS OVER ADAMS PLATINUM CATALYST WITH CERTAIN OXIME-ACETIC ACID SOLUTIONS

Solute	Concn., moles/l.	Exchange, %
Methyl ethyl ketoxime	0.1	27.3
	0.6	35.9
	1.0	37.1
	2.0	39.8
Phenylacetaldoxime	0.0015	30.9
	.0045	30.2
	.0075	38.2
	.015	43.5
	.030	42.4
Methyl ethyl ketoxime (0.1 M) plus aniline (0.1 M)		38.5
Methyl ethyl ketoxime (0.1 M) plus water (0.1 M)		35.5

Discussion

In contrast to the behaviors of nitrobenzene, which prevented the exchange, and nitroethane, which had no effect upon the exchange, 2-nitro-1-butene increased it markedly in solutions of low

concentration. This effect passed through a maximum, and in solutions of high concentration no exchange was detected. This was found to be true for *β*-nitrostyrene as well. The maxima observed in the exchange curves for these nitro olefins indicate that the reduction of the nitro group is competing with the exchange of deuterium and acetic acid. In low concentrations of nitro olefin the rate of exchange is greatly accelerated, indicating either that insufficient nitro olefin is present to completely occupy the catalyst surface and exchange is taking place on the portion of the surface which is not covered by adsorbed nitro olefin molecules, or the nitro group is reduced first and then desorbed to yield a species which increases the rate of exchange.

If the former possibility were the case, the exchange shown by these systems should be less than that shown by pure acetic acid over the catalyst when no other compound is interfering with the exchange. In neither case did the initial portion of the exchange curve fall below that value exhibited by pure acetic acid. Previous evidence¹ indicates that even in dilute solutions of nitro compounds the catalytic surface is covered with a monolayer of adsorbed nitro molecules.

The latter possibility is supported by several pieces of evidence. In the higher concentration nitro olefin solutions the rate of exchange fell off rapidly, and most of the deuterium gas was absorbed by the system during the three minutes of reaction, indicating that the reduction of the nitro group was proceeding rapidly. On the basis of the latter possibility, this is expected, for in these systems which contain more nitro olefin, a longer period of time and more deuterium gas would be required for complete deuteration of the nitro compound. Also, if these systems which showed little or no exchange were allowed to react with deuterium for a sufficient period to reduce all of the nitro olefin, these systems should exhibit an increased rate of exchange after the reduction of the nitro group. This was found to be so.

Successive portions of deuterium were added to two different concentrations of *β*-nitrostyrene in acetic acid and successive three-minute exchanges carried out with analysis of the gaseous phase between the addition of deuterium samples. The results are shown in Table III.

TABLE III

REACTION OF *β*-NITROSTYRENE SYSTEMS WITH DEUTERIUM GAS

Initial concn., mole/l.	Total exchange time, min.	Exchange (%) during last 3-min. interval
0.03	3	38.8
.03	6	50.5
.03	9	39.2
.1	3	8.1
.1	6	32.7
.1	9	48.3
.1	12	46.5
.1	15	44.2

In both cases there was a rapid uptake of deuterium, which became less with the addition of successive samples of deuterium, and an intense green

color was imparted to the solution. The amount of exchange was small following the first three minutes of reaction, but soon increased to a level somewhat above the maximum exhibited in the previously determined exchange curve for β -nitrostyrene (see Table I), and then decreased slowly. The strong adsorption of the nitro compound controls the reaction, reduction taking place first, and then the exchange reaction comes into prominence after the nitro compound has been reduced. The reduction and the exchange are both rapid under these conditions.

The oximes did increase the rate of exchange initially above that shown by acetic acid, but after a given level of exchange was attained the addition of more material failed to increase further the rate of exchange. The final level reached by the oximes in each case was lower than the maximum exhibited by the parent nitro compound. Since in the reduction of nitro compounds, an amine and water are also formed,² equimolar solutions of oxime-aniline and oxime-water in acetic acid were studied (see Table II). The oxime-aniline solution exhibited more exchange than did the oxime-water solution, although the exchange in each case was greater than that exhibited by a solution of oxime of the same concentration.

This indicates that in the reduction the α,β -unsaturated nitro compounds probably go through oxime intermediates which then increase the rate of exchange. There was sufficient methyl ethyl ketoxime present to furnish all of the hydrogen found in the gaseous phase, but for phenylacetaldoxime this was not the case so that some of the hydrogen must have come from the acetic acid. There was no color formation during the exchanges involving the oxime-acetic acid systems.

The reaction of a nitro group with hydrogen over a catalyst is greatly affected by the remainder of the molecule. The nitro group in nitromesitylene is attached to an aromatic ring which would indicate that this compound should prevent the exchange as does nitrobenzene. However, the two methyl groups *ortho* to the nitro group reduce the resonance interaction of the nitro group with the benzene ring. Thus the kinetics of the catalytic hydrogenation of nitromesitylene are somewhat different from those for the hydrogenation of nitrobenzene. The lack of interaction of the nitro group with the ring results in a nitro group which in reactivity somewhat resembles one found in an aliphatic compound. Nitromesitylene in solutions of low concentrations decreased the rate of exchange, resembling nitrobenzene, but in solutions of higher concentrations nitromesitylene failed to change further the rate of exchange.

Although the behavior of aniline is similar to that of nitromesitylene different considerations apply. The hydrogenation of aniline over Adams platinum catalyst in acetic acid is zero order with respect to aniline, as is the hydrogenation of nitrobenzene. Aniline, however, is less strongly adsorbed than is nitrobenzene and hence has less effect on the exchange. The fact that nitrobenzene undergoes hydrogenation initially to form aniline which is then desorbed has been shown in previous studies. When all of the nitrobenzene is hydrogenated, the aniline is readsorbed and the benzene ring hydrogenated to give cyclohexylamine.

Acknowledgment.—The authors are indebted to the United States Atomic Energy Commission for support of this work.

KNOXVILLE, TENNESSEE

[CONTRIBUTION FROM THE HOUDRY PROCESS CORPORATION]

Reactions of C₅-C₈ Paraffins with a Silica-Alumina Cracking Catalyst.¹ I. Isomerization

BY S. G. HINDIN, A. G. OBLAD AND G. A. MILLS

RECEIVED JULY 23, 1954

The interaction of C₅-C₈ paraffins with a silica-alumina cracking catalyst at 100-150° was studied by measurement of isomerization and cracking. It was found that two factors are critical if isomerization and cracking are to occur; one, the degree of catalyst hydration, and two, the structure of the hydrocarbon molecule. Small amounts of water added to the highly dehydrated catalyst activate, and larger amounts inactivate the catalyst. Only paraffin molecules possessing a tertiary carbon atom undergo reaction at these conditions; monomethyl and dimethyl paraffins (with methyl groups on separate carbon atoms) show extensive isomerization, whereas normal paraffins and those molecules containing only the quaternary structure show no reaction. With highly branched structures, cracking becomes the predominant reaction, with isobutane the major product.

It has long been observed that cracking catalysts are not isomerization catalysts for paraffins at the usual cracking conditions. For example, Good, Voge and Greensfelder² found, from studying the cracking of the isomeric hexanes at 550° and 0.5 LHSV, direct isomerization of hexanes was of small importance, for only in the reaction with 2,3-

dimethylbutane was isomerization apparent (approximately 6% of charge). Unpublished data from this Laboratory and data given by Hansford³ on the reaction of normal butane at cracking conditions similarly disclosed no evidence of isomerization. Pines, in his chapter in "Advances in Catalysis,"⁴ stated, "The isomerization in the presence of the oxide catalysts proceeds usually at high temperatures and in the presence of hydrogen.

(1) Presented before the Petroleum Division, American Chemical Society, March, 1953.

(2) G. M. Good, H. H. Voge and B. S. Greensfelder, *Ind. Eng. Chem.*, **39**, 1032 (1947).

(3) R. C. Hansford, *ibid.*, **39**, 849 (1947).

(4) H. Pines, *Advances in Catalysis*, Vol. I (1948).