

form and undergoes hydrogen bonding on solution, thus giving rise to a different absorbing entity in solid than in solution. It will be further noted that no band shorter than 3.2 occurs for isocytosine, which would indicate the presence of a free NH rather than a free NH<sub>2</sub> group. This is substantiated by the failure of isocytosine to react with nitrous acid.

It is hoped that by extending the compounds investigated in solid potassium bromide, to arrive at some empirical values which may be used in analysis for concentration in mixtures and crude preparations of extracts.

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## The Influence of Nitro Compounds on the Catalytic Exchange Reaction Between Deuterium Gas and Acetic Acid. Evidence for the Mechanism of the Catalytic Hydrogenation of Nitro Groups

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Studies of the kinetics of exchange between deuterium and glacial acetic acid in the presence of Adams platinum catalyst indicate that the reaction is first order with respect to the deuterium pressure and essentially zero order with respect to acetic acid concentration (in *n*-heptane over range 10–100%) and has an activation energy of about 13,600 calories. The exchange reaction is completely suppressed by the addition of a small amount of nitrobenzene, but is unaffected by the addition of nitroethane. In either case, the nitro group is deuterated to form the amine. The results are discussed in the light of the mechanism of catalytic exchange and catalytic hydrogenation reactions.

Previous studies of the hydrogenation of nitro groups have shown that nitrobenzene undergoes hydrogenation on Adams platinum catalyst in the presence of glacial acetic acid at a rate which is zero order with respect to the concentration of acceptor, but proportional to the hydrogen pressure. For nitroethane, and nitroalkanes in general, the kinetic behavior is reversed.<sup>3</sup> The rate of this reaction is essentially independent of the hydrogen pressure, but directly proportional to the concentration of the nitroethane in the acetic acid solvent. For both compounds the nitro group is reduced to form the amine.

The catalytic exchange between deuterium gas and glacial acetic acid containing these two acceptors has been studied with a view to obtaining further information regarding the kinetics of these two hydrogenation reactions.

### Experimental

**Materials.**—du Pont C.P. glacial acetic acid, nitrobenzene and nitroethane were purified as in previous work.<sup>3</sup> Adams platinum catalyst was prepared from C.P. platinum chloride by the usual method.<sup>4</sup> That which passed a 325-mesh screen was used for the exchange experiments. Research grade *n*-heptane (99.87 mole per cent.) was purchased from the Phillips Petroleum Company.

Preliminary experiments with this material indicated an impurity containing exchangeable hydrogen which was no longer detected after prolonged shaking with hydrogen gas and platinum catalyst. Accordingly, the solvent was pretreated in this manner before use.

Hydrogen gas was obtained from the National Cylinder Gas Company and deuterium gas (minimum purity 99.5 per cent.) from the Stuart Oxygen Company. Both were used without further purification. Pure hydrogen for use in standardizing the analytical apparatus was obtained by liberation with clean J. T. Baker C.P. metallic sodium from glacial acetic acid.

**Exchange Apparatus and Procedure.**—The apparatus used for the exchange studies consisted of a 50-ml. erlenmeyer flask, the opening of which was extended by sealing on a 12-cm. length of 10-mm. tubing. One side of a two-way, straight-bore stopcock (size 6) was sealed to this unit at a point 3 cm. below the barrel. On the opposite side there was attached a socket from a standard ball and socket joint assembly. The volume of the reaction flask to the stopcock was about 67 ml.

Exchange studies were made by introducing the requisite liquids and platinum oxide through a funnel which extended through the bore of the stopcock, and evacuating the flask while it was cooled in a Dry Ice-acetone-bath. The flask was then warmed to room temperature, shaken for a few minutes, and recooled in the Dry Ice-acetone mixture. It was again evacuated, warmed to the requisite temperature, and filled with deuterium. The second evacuation was necessary in order to remove dissolved gases from the liquid. The reaction flask and contents were then placed in a jacket attached to a cradle and shaken for a definite period of time, usually three minutes. The temperature of the circulating water in the jacket was held to  $\pm 0.2^\circ$ . The shaker was usually operated at about 350 cycles per minute; this was sufficient to ensure equilibrium conditions. Finally the flask was removed from the cradle and attached to the analytical apparatus by means of the ball and socket joint.

Preliminary experiments at 30° with 7 mg. of prerduced catalyst showed no exchange over a ten-minute period of time in the absence of shaking; hence some delays could be tolerated at this temperature in the handling of the mixtures before and after shaking. At 43°, however, some 16% exchange did occur on 7 mg. of prerduced catalyst over the same time interval. In the study of the temperature-dependence of the exchange, therefore, the contents were warmed to the requisite temperature before adding deuterium and placed in the jacket and shaken without delay. Within about 30 seconds the circulating water in the jacket came to the required temperature. At the end of the shak-

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(3) H. A. Smith and W. C. Bedoit, *J. Phys. Colloid Chem.*, **55**, 1085 (1951).

(4) R. Adams, V. Voorhees and R. L. Shriner, *Org. Syntheses*, **8**, 92 (1928).

ing time the flask was plunged into the freezing mixture within 30 seconds.

**Analyses.**—The analytical apparatus consisted of a manifold leading through stopcocks to the reaction flask, hydrogen gas, deuterium gas, vacuum pump, manometer and analysis bulb. One end of the analysis bulb, of about 10-ml. capacity, was connected to the manifold through the opposite ends of a three-way stopcock, while the other end of the bulb was connected to a reservoir containing mercury. A cold trap, surrounded by Dry Ice-acetone mixture, was placed between the analysis bulb and the manifold. Rubber connections were kept at a minimum and isolated during the analysis.

After the manifold was evacuated, a representative sample of the gases was drawn into the bulb, isolated from the manifold with the three-way stopcock, and allowed to pass through a pin-hole (0.02 mm. dia.) pierced in platinum foil (0.001 in. thick) sealed to the stub of the remaining arm of the stopcock. The time of the passage of the mercury under a fixed average pressure and at a given temperature between two marks on capillary tubing sealed to opposite ends of the bulb were measured. Effusion times were of the order of 100 seconds for pure hydrogen liberated from pure acetic acid with sodium and 140 seconds for tank deuterium ( $t_{D_2}/t_{H_2} = 1.406$ ). For a given sample of gas and at a fixed temperature ( $\pm 1^\circ$ ) these times could be reproduced with a precision of one part per thousand. Isotopic percentages, therefore, could be measured to about five parts per thousand. Atomic percentages were computed by means of the formula

$$\text{Atomic per cent. H} = \frac{(t_{D_2}^2 - t_x^2)/(t_{D_2}^2 - t_{H_2}^2)}{(M_{D_2} - M_x)/(M_{D_2} - M_{H_2})}$$

where  $t_{D_2}$ ,  $t_{H_2}$  and  $t_x$  are the effusion times of deuterium, hydrogen and isotopic mixture, respectively, and where  $M_{D_2}$ ,  $M_{H_2}$  and  $M_x$  are the corresponding molecular weights. This relation was derived from Graham's law of effusion. It was assumed that any isotopic mixture has the same effusion time as that of a hypothetical diatomic molecule having a molecular weight equal to the average molecular weight of the mixture. This is equivalent to saying that no fractionation occurs. To test the equation, effusion times were measured for known mixtures (determined manometrically) of tank hydrogen and deuterium and the percentages compared with the values calculated from their effusion times using the above equation. The following percentages using standard mixtures made up manometrically (compositions given in parentheses) were obtained: 27.6 (27.7), 28.3 (28.3), 50.1 (49.5), 57.9 (57.3), 62.8 (62.6) and 68.7 (68.8). One should note in particular that the equimolecular mixture of  $H_2$  and  $D_2$  gave essentially the same effusion time as that which would be predicted for HD on the basis of the above equation. It follows, therefore, that in the effusion apparatus all mixtures of  $H_2$ ,  $D_2$  and HD having the same D/H ratio should give essentially the same effusion time. It was found that the ratio using tank hydrogen  $t_{D_2}/t_{H_2} = 1.364$  was constant over several degrees of room temperature. This lower value probably reflects the presence of oxygen in the tank hydrogen.

Other errors in experiment were greater than those of analyses. Chief among these was catalyst inhomogeneity in the very small quantities used.

Blank runs, made from time to time with hydrogen (or deuterium in the absence of catalyst) indicated no leakage of air into the apparatus. This was indicated also by the complete absence of upward trends in the time values as successive samples were withdrawn for analysis. All reaction flasks used were tested for leakage of air into them by analysis of hydrogen admitted to the flasks after they had stood evacuated for one hour or longer.

**Hydrogenation Apparatus.**—Hydrogenation experiments were carried out in a low-pressure Parr reduction apparatus, or at atmospheric pressure in an apparatus similar to that used for the exchange studies. In the latter apparatus the pressure was followed with a manometer. The procedure was similar to that previously described.<sup>3</sup>

### Experimental Calculations and Results

Preliminary experiments indicated that the rate of exchange of deuterium with glacial acetic acid for shaking rates of 490 cycles per minute was proportional to the weight of platinum oxide added up to ten milligrams. No exchange

could be detected in the absence of the catalyst. Further experiments indicated that when six milligrams of catalyst was employed, the exchange was independent of the shaking speed within the range 330-480 cycles per minute. Subsequent experiments were carried out with six milligrams or less of catalyst, and shaking speeds within the range indicated.

The rate of exchange was found to be proportional to the initial deuterium pressure, as may be seen from Fig. 1. The first order dependence of the rate on the atomic per cent. of deuterium in the gas was shown by the fact that plots of this quantity against time gave straight lines.

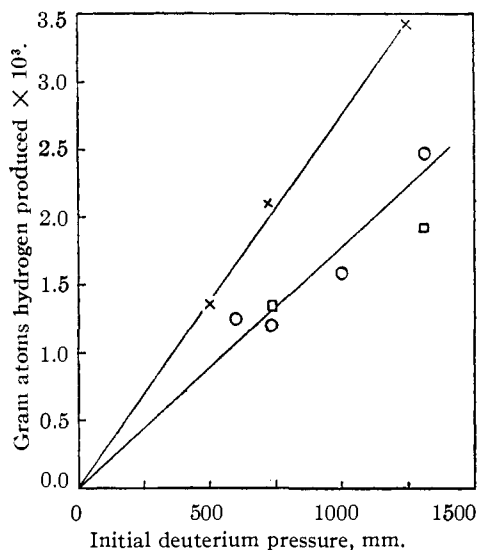


Fig. 1.—Effect of pressure on rate of exchange at  $30^\circ$  of  $D_2$  with acetic acid, O; with 1% (by volume) nitroethane in acetic acid, □; and with 60% acetic acid in *n*-heptane, X. Reaction time, 3 min.; 6 mg. platinum oxide.

Most of the exchange experiments were carried out using acetic acid alone. Some studies were made with *n*-heptane as a diluent, so that the reaction order with respect to the concentration of acetic acid could be established. The results, shown in Fig. 2 exhibit some increase in exchange rate as the acid is diluted. This may be caused by a decreased surface tension of the liquid, or perhaps by self-poisoning due to unusually strong adsorption of acetic acid. In any case it appears that acetic acid is more strongly adsorbed than is hydrogen. Erratic results were found in solutions less than 10% with respect to acetic acid. These are believed to be due to lack of wetting of the catalyst by the

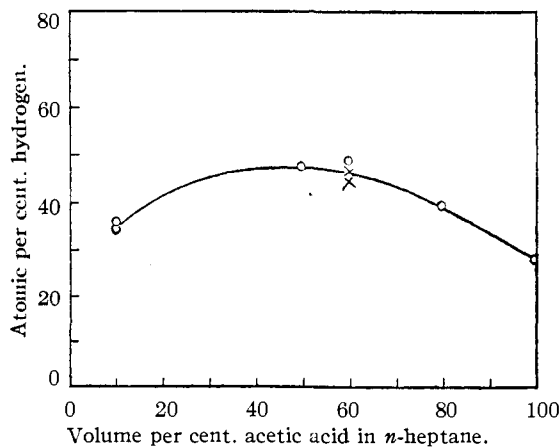


Fig. 2.—Variation with per cent. acetic acid in *n*-heptane of exchange with  $D_2$  (1 atm.) on platinum at  $30^\circ$ ; 6 mg. platinum oxide; 3 minutes shaking; X runs at 500 and 1300 mm.  $D_2$  pressure.

solution, and to sticking of catalyst particles to the wall of the reaction vessel. Since this range is of little importance in establishing the reaction order with respect to the concentration of acetic acid near 100%, these data are omitted from the graph. Data shown in Fig. 1, for a mixture containing 60% acetic acid, again indicate that the reaction is first order with respect to the deuterium pressure.

The influence of temperature on the exchange reaction is shown in Fig. 3. The activation energy calculated from these data is approximately 13,600 calories per mole. The reaction rate constants were computed from an integrated form of the relation  $-d(D)/dt = k(D)$ , wherein (D) is atomic per cent. of deuterium,  $t$  is the time, and  $k$  is the reaction rate constant.

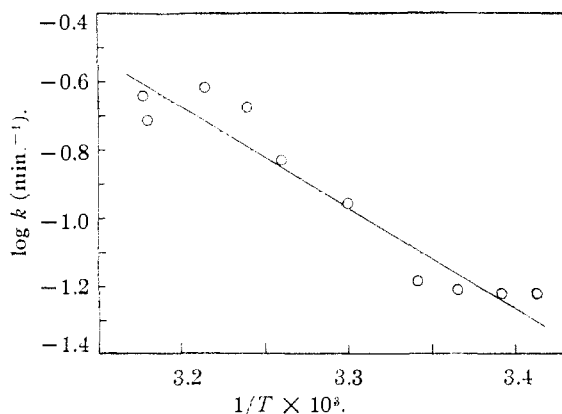


Fig. 3.—Activation energy plot for exchange of  $D_2$  with acetic acid on platinum; reaction time 3 minutes; 6 mg. platinum oxide;  $E = 13,600$  cal./mole.

The effects on exchange of adding nitrobenzene and nitroethane are shown in Table I. When nitrobenzene was added to the acetic acid in amounts as small as 0.1 ml. per 10 ml. of acetic acid, no exchange took place over a period of three minutes. During that same period of time, about 35% of the nitrobenzene was reduced, using up some 30% of the deuterium originally present. When the experiment was repeated using only 0.01 ml. of nitrobenzene, exchange did take place. However, this was presumably caused by the complete reduction of the nitrobenzene to aniline within a period of about one minute.

The addition of as much as 50% of nitroethane to the acetic acid did not materially influence the exchange reaction. With a solution consisting of 1 ml. of nitroethane in 10 ml. of solution, the exchange was found to be proportional to the hydrogen pressure and essentially equivalent to the exchange of deuterium with acetic acid alone, as may be seen from Fig. 1.

When nitroethane alone was shaken with deuterium in the presence of platinum, about one-fourth as much exchange was found as when acetic acid was also present. In the latter mixture the acid medium would be expected to essentially eliminate even this exchange between deuterium and nitroethane since the *aci*-form of nitroethane would be greatly suppressed. In addition, the acetic acid is evidently more strongly adsorbed on platinum than the nitroparaffin.

TABLE I

DEUTERIUM EXCHANGE ON PLATINUM OF SOLUTIONS OF NITROBENZENE AND NITROETHANE IN GLACIAL ACETIC ACID AT  $30^\circ$ , AFTER SHAKING FOR THREE MINUTES WITH 0.006 G. OF PLATINUM OXIDE

Solute	Ml. solute/10 ml. solution	Atomic per cent. H
Acetic acid only	0.00	28.3
Nitrobenzene	0.01	20
Nitrobenzene	0.10	0
Nitrobenzene	1.0	0
Nitroethane	0.1	30.5
Nitroethane	1.0	29.1
Nitroethane	5.0	29.4

## Discussion

The hydrogenation studies reported earlier<sup>3</sup> indicated the following order of adsorption on Adams platinum catalyst: nitrobenzene > hydrogen > nitroethane. The exchange studies are in line with this result, since nitrobenzene prevents the deuterium exchange while nitroethane does not. Presumably the nitrobenzene excludes either the hydrogen or the acetic acid from the catalyst surface. If one assumes that the deuterium is adsorbed in gaps in a nearly complete monolayer of nitrobenzene, in order to explain the rapid deuteration of the nitro group, one must assume that the acetic acid is excluded since no exchange is found. However, the exchange results indicate that acetic acid is much more strongly adsorbed than deuterium under the experimental conditions employed. Therefore, if deuterium is adsorbed in gaps in a nitrobenzene monolayer to the extent required for the deuteration reaction, the more strongly adsorbed acetic acid should be present in sufficient quantity to indicate some exchange. Lack of such exchange, even when deuteration is taking place at a rapid rate, appears to support the theory that during the deuteration the nitrobenzene is present as a full monolayer on the platinum surface, while the deuterium is not so adsorbed, but rather comes from the liquid phase or from a weakly adsorbed van der Waals layer. In this case, support for a Rideal type mechanism<sup>5</sup> rather than for a Langmuir-Hinshelwood type<sup>6</sup> is indicated.

If the deuteration of nitrobenzene in acetic acid were much faster than the exchange reaction when nitrobenzene is absent, one might conclude that the exchange reaction should not be detected. However, this is not the case, as may be seen from Fig. 4, in which the rates of deuteration and ex-

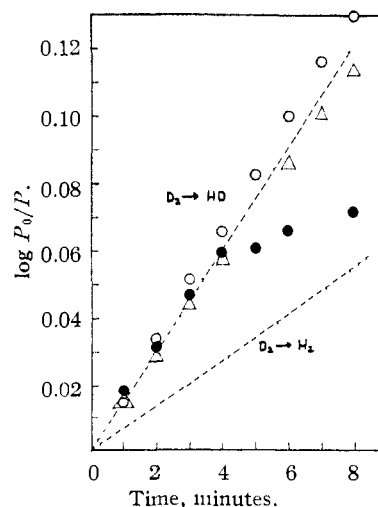


Fig. 4.—Comparison of rates of (1) exchange of  $D_2$  with acetic acid (broken lines) and (2) deuteration of nitrobenzene in acetic acid: O, 10% nitrobenzene by volume (50 ml. total);  $\Delta$ , 1%;  $\bullet$ , 0.2%.

(5) E. K. Rideal, *Proc. Cambridge Phil. Soc.*, **35**, 130 (1939); D. D. Eley, *Quart. Revs. (London)*, **3**, 213 (1949).

(6) I. Langmuir, *Trans. Faraday Soc.*, **17**, 607 (1921); C. N. Hinshelwood, "The Kinetics of Chemical Change," Oxford, 1940, p. 187; K. J. Laidler, *J. Phys. Colloid Chem.*, 1067 (1951); "Chemical Kinetics," First Edition, McGraw-Hill Book Company, Inc., New York, N. Y., 1950, p. 152.

change are compared. For deuteration,  $P_0$  and  $P$  represent starting pressure and pressure at time  $t$ , respectively; for exchange  $p_0/P$  is equal to  $P_{0D_2}/P_{D_2}$ , wherein  $P_{0D_2}$  and  $P_{D_2}$  are initial pressure and pressure at time  $t$ , respectively, of the  $D_2$  species. Since the analytical method takes no cognizance of species, it was necessary to consider two extreme cases for evaluating the pressure of  $D_2$  at time  $t$ : (1) that all the measured exchange is due to the conversion of  $D_2$  to  $H_2$ , and (2) that the measured exchange represents only the conversion of  $D_2$  to HD. Consideration of these cases gives two possible extremes for the disappearance of  $D_2$  with time, as indicated by the two broken lines of Fig. 4. The upper one coincides with the experimental points for deuteration. Since the utilization of  $D_2$  to form HD is preponderant in the early stages of the exchange, it is quite likely that the disappearance of  $D_2$  is represented more nearly by the upper one, so that consumption of  $D_2$  in deuteration proceeds at about the same rate as the consumption of  $D_2$  in exchange with pure acetic acid. Therefore, if the two reactions were competing for deuterium in the ordinary kinetic sense, one should have had no difficulty in detecting the exchange process.

The fact that the deuterium pressure falls off during the reduction reaction does not mean that the measured exchange, expressed as atomic per cent. hydrogen, would be correspondingly diminished. On the contrary, if both reactions were occurring at the same rate, the atomic per cent. hydrogen should not change at all, since this

quantity is independent of the pressure. This statement follows directly from the data of Fig. 1. Since the exchange reaction is somewhat slower than the deuteration reaction, the atomic per cent. hydrogen might diminish somewhat, but should certainly be detected if the two reactions were competing.

In the presence of nitroethane, the exchange of deuterium with acetic acid proceeds unhindered, since the acetic acid in this case can become chemisorbed on the catalyst surface and exchange with the deuterium.

While the hydrogenation of nitrobenzene appears to be better explained by a mechanism of the Rideal-Eley type, the mechanism of the hydrogenation of nitroethane is not apparent from the exchange studies. It does appear that hydrogenation and exchange in this case are taking place independently of each other, inasmuch as hydrogenation is independent of the gas pressure, while deuterium exchange is proportional to the first power of that pressure. This might appear to constitute an anomaly, since in the hydrogenation reaction the hydrogen may be presumed to be strongly adsorbed on the catalyst surface, while in the exchange reaction it is presumably weakly adsorbed. However, this may indicate that the reactions occur on different catalyst sites, or may be a consequence of the fact that acetic acid is much more strongly adsorbed than hydrogen while the hydrogen, in turn, is more strongly adsorbed than the nitroethane.

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[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

## Ketene Acetals. XXVI. The Preparation and Properties of Some $\omega$ -Cyanoalkylketene Acetals

BY S. M. McELVAIN AND RICHARD D. MULLINEAUX<sup>1</sup>

De-alcoholation of the  $\omega$ -cyano-orthoesters III, IV and V with aluminum methoxide yields the corresponding  $\omega$ -cyano-ketene acetals VI, VII and VIII, exclusively. The alternative cyclic structures of the type of IX were eliminated as possible de-alcoholation products by hydrolysis of VII and VIII to the respective normal esters and by the conversion of VI to carbomethoxycyanomethylketene acetal (X) with chloroformic ester; this reagent converts other ketene acetals smoothly to the corresponding carbalkoxyketene acetals (XIII). Sodium methoxide is shown to be a catalyst for the de-alcoholation of methyl  $\delta$ -cyano-orthovalerate (V) to the ketene acetal VIII. Further reaction of VIII with this base yields initially 1-methoxy-2-cyanocyclopentene-1 (XVII), which then suffers cleavage to 2-cyanocyclopentanone (XVIII) and dimethyl ether. The relationships between the boiling points of these  $\omega$ -cyanoketene acetals and the corresponding normal and orthoesters are pointed out.

The facile pyrolysis of methyl orthocyanacetate to methanol and cyanoketene dimethylacetal was reported<sup>2</sup> in Paper XX of this series. In contrast to the behavior of this orthoester, the homologous methyl ortho- $\beta$ -cyanopropionate (III) when subjected to pyrolysis lost methanol quite slowly and was converted to a tar.<sup>3</sup> It seemed of interest to investigate the de-alcoholation of the latter orthoester, as well as the homologous compounds IV and V, with the aluminum alkoxides, which recently

have been found<sup>4</sup> to be efficient catalysts for the conversion of orthoesters to ketene acetals. Aside from a further extension of this method of de-alcoholation, there was the possibility that the hydrogen in the  $\alpha$ -position to the cyano group might be involved in the de-alcoholation with the production of an alicyclic ketal such as IX instead of a ketene acetal.

Each of the  $\omega$ -cyano-orthoesters III, IV and V, which was readily prepared from the corresponding dinitrile I *via* the iminoester hydrochloride (II), was readily de-alcoholated at 250° with 30 mole per cent. of aluminum methoxide to the ketene

(1) E. I. du Pont de Nemours and Company Research Assistant 1951.

(2) S. M. McElvain and J. P. Schroeder, *THIS JOURNAL*, **71**, 47 (1949).

(3) *Ibid.*, **71**, 40 (1949); J. P. Schroeder, Ph. D. Thesis, University of Wisconsin, 1948.

(4) S. M. McElvain and (a) J. T. Venerable, *THIS JOURNAL*, **72**, 1661 (1950); (b) W. R. Davie, *ibid.*, **73**, 1400 (1951).