

of isotopic fractionation) requires comment, since usually bond-breaking reactions will show an isotope effect. It seems likely that this step does indeed require activation energy, since the relative yields of olefin and alkyl halide are temperature sensitive, suggesting that the elimination process has an activation energy about 780 cal. higher than the displacement process. The consequence of this observation is that the sum of the zero point energies of vibration of the carbon-hydrogen bonds must be unchanged on going from the carbonium ion to the transition state. Two explanations can be offered for this lack of detectable isotope effect. In the first, consideration may be given not only to the bond which is being broken, but to all the other bonds as well. Thus if the weakening of all 5 bonds to β -hydrogens were the same, a reduction in the zero point energy of one of these to zero might be compensated by an increase in the zero point energy

of the other four, and this compensation could be exact if the force constants in the carbonium ion were only 64% of those in the second transition state. The second explanation is based on the assumption that the force constant of the bond to be broken is not much reduced in the transition state going to the olefin. This implies that the small activation energy arises from some other source than the process of breaking this bond. It is probably not necessary to look for an explanation predicting an identically zero isotope effect; we are more inclined to believe that an effect may be present, but is in this case very small.

Thus the unexpected results with the deuterium compound confirm the carbonium ion nature of the reaction and the participation of the solvent dioxane; furthermore, the elimination reaction also goes by way of the same carbonium ion.

HOUSTON, TEXAS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE RICE INSTITUTE]

The Decomposition of Secondary Alkyl Chlorosulfites. IV. The Tertiary Amine Catalysis¹

BY EDWARD S. LEWIS AND GALVIN M. COPPINGER

RECEIVED AUGUST 10, 1953

The decomposition of secondary alkyl chlorosulfites is catalyzed by tertiary amines and their hydrochlorides. A kinetic study of the reaction of isopropyl chlorosulfite in dioxane solution shows that the reaction follows a first-order course, with the apparent first-order rate constants increasing linearly with the concentration of catalyst. A bimolecular displacement of the S_N2 type between chloride ion and the chlorosulfite is proposed, which is consistent with the kinetics, the stereochemical result, the order of efficacies of the various catalysts and the magnitude of rate retardation with deuterium substitution in the β -positions. In the case of catalysis by the free amines, chloride ion is believed to arise from a prior elimination reaction. A positive salt effect is present, but is not alone responsible for the increase in rate on adding amine hydrochlorides.

Introduction

There are several examples of the profound effect of pyridine on the steric course of the reaction of alcohols with thionyl chloride.²⁻⁴ Gerrard has attributed this effect to a catalysis of the decomposition of chlorosulfite by pyridine hydrochloride, which he was able to observe in a heterogeneous system.⁵ It has also been shown that dilute solutions of pyridine hydrochloride in dioxane gave from secondary alkyl chlorosulfites an extensively inverted alkyl chloride, although configuration is retained in the absence of this salt.⁶

The studies here reported were designed to clarify the function of the base in this catalyzed decomposition. The experiments were carried out in dioxane solution since the change in stereochemical result in this solvent on adding the amine provides an additional criterion for the detection of catalysis. In most of the experiments, however, isopropyl chlorosulfite was used, because it is the most readily distillable secondary chlorosulfite, and because it was hoped that elimination would

account for a smaller fraction of the product than in the other cases where a disubstituted ethylene could be produced.

Experimental

Materials.—Dioxane was boiled under reflux with sodium metal for 24 hours and distilled through a packed column. The fraction collected boiled at $101 \pm 0.5^\circ$ and was further purified by partial freezing, the frozen material only was used. This fractional freezing was repeated if necessary. Purity was estimated by measurement of the optical density compared to air at 230 $m\mu$. The average optical density was 0.350, the extreme values were 0.200 and 0.450.

The tertiary bases were commercial products purified by distillation. Pyridine hydrochloride was prepared *in situ* by mixing dioxane solutions of pyridine with the calculated amount of a solution of hydrogen chloride in dioxane, standardized by titration.

Methylpyridinium chloride was prepared from the iodide by treatment with an aqueous silver chloride suspension. The iodide was prepared in the usual manner from pyridine and methyl iodide. Propylpyridinium chloride was prepared from pyridine and *n*-propyl chloride by heating in a closed flask. Both salts were recrystallized from a propyl ether-propyl alcohol mixture.

Lithium perchlorate was prepared from lithium carbonate and 70% perchloric acid. After removing the water under vacuum, the resulting trihydrate was recrystallized from ethanol. The trihydrate was dehydrated by heating at 100° and 0.5 mm. pressure for one hour.

The preparation of the chlorosulfite followed the previously described methods,⁶ using alcohols prepared in the same work.^{6,7} Isopropyl alcohol was purified by distillation; it gave a chlorosulfite boiling at $39-40^\circ$ at 20 mm.

(1) Presented in part at the Los Angeles Meeting of the American Chemical Society, March, 1953.

(2) J. Kenyon, A. G. Lipscomb and H. Phillips, *J. Chem. Soc.*, 415 (1950).

(3) J. Kenyon, H. Phillips and F. M. H. Taylor, *ibid.*, 382 (1951).

(4) H. C. Stevens and O. Grummitt, *THIS JOURNAL*, **74**, 4876 (1952).

(5) W. Gerrard, *J. Chem. Soc.*, 99 (1949).

(6) C. E. Boozer and E. S. Lewis, *THIS JOURNAL*, **75**, 3182 (1953).

(7) C. E. Boozer and E. S. Lewis, *ibid.*, **76**, 794 (1954).

Kinetic Measurements.—The previously described spectrophotometric method was only slightly modified. The same type of apparatus was used, but the sample of the reaction mixture which varied from 10 to 25 microliters was diluted to 10.0 ml. with dioxane instead of isoöctane for measurement of optical density. This appeared to be necessary to keep the amine hydrochlorides in solution, since dilution with isoöctane caused precipitation of pyridine hydrochloride inside the cells, and there appeared to be a catalysis of chlorosulfite decomposition at the surfaces so produced. The optical density of these dioxane solutions decreased perceptibly with time, possibly because of water absorption, so readings were taken at one-minute intervals for five minutes, and the values were then extrapolated back to the time of removal of the sample from the reaction vessel.

Solutions of the bases were made up volumetrically, except in some cases where the concentration of base was determined spectrophotometrically using the wave length of maximum absorption. Solutions of the quaternary chlorides were made up gravimetrically, with some error introduced by the hygroscopic nature of these salts. The solutions used were very nearly saturated, thus the rather low accuracy of the derived second-order rate constant could not be improved by raising the concentration.

The calculation of rate constants was accomplished by the method of Guggenheim,⁸ since it automatically cancels the effect of a constant residual absorption due to the catalyst. However, a significant residual absorption not attributable to catalyst was nearly always present; this is one of the limiting factors in the accuracy of the results, but this limitation does not appear to be serious.

Product Isolation.—The isolation of 2-chlorobutane followed the previously described procedure.⁹ Isopropyl chloride was isolated by a similar technique from the decomposition in dioxane solution of isopropyl chlorosulfite in the presence of 5×10^{-3} M pyridine in a yield of 61%. The yield is unquestionably reduced by the high volatility of the chloride. No attempt was made to isolate propene.

Results

In any one run the decomposition followed a first-order course, but the apparent first-order rate constant (k_{app}) depended on the concentration of

TABLE I
RATE OF CATALYZED DECOMPOSITION OF ISOPROPYL CHLOROSULFITE

Catalyst	Concn. moles/l. $\times 10^3$	Temp., °C.	$k_{app} \times 10^4$
None	...	39.8	0.23
Pyridine	3.80	39.8	1.0
Pyridine	5.06	39.8	1.4
Pyridine-HCl	2.10	39.8	0.610
Pyridine-HCl	6.50	39.8	1.8
Pyridine-CH ₃ Cl	0.035	39.8	0.33
Pyridine-C ₃ H ₇ Cl	0.056	39.8	.40
LiClO ₄	10.9	39.8	.65 ^a
LiClO ₄	10.9	39.8	.24 ^b
Pyridine-HClO ₄	0.850	39.8	.27
None	...	52.9	.678
Pyridine	1.24	52.9	1.90
Pyridine	2.48	52.9	3.23
Pyridine	3.72	52.9	4.18
Pyridine	4.96	52.9	4.98
Pyridine	6.23	52.9	5.66
Quinoline	3.72	52.9	3.02
Dimethylaniline	3.72	52.9	1.95
2,6-Lutidine	3.72	52.9	4.68
LiClO ₄	1.00	52.9	0.896
LiClO ₄	5.50	52.9	0.988
LiClO ₄	10.3	52.9	1.17

^a Initial chlorosulfite concentration = 0.07 M. ^b Initial chlorosulfite concentration = 0.35 M.

(8) E. A. Guggenheim, *Phil. Mag.*, [7] 2, 538 (1926).

(9) E. S. Lewis and C. E. Boozer, *THIS JOURNAL*, 74, 308 (1952).

catalyst. Table I lists the values obtained in the presence of various substances. The data at 39.8° are less accurate than those at 52.9°, and none are as accurate as those reported for the uncatalyzed reaction.⁶

At high lithium perchlorate concentration (0.01 M) at 39.8°, the first-order plots were not very good, but constants were nevertheless calculated and reproduced. Contribution of a lower order reaction is suggested by the observation that there was a more than twofold reduction in this constant with a fivefold increase in the initial chlorosulfite concentration. However treatment of these runs as one-half order was less satisfactory than the first-order treatment. None of the other runs with lithium perchlorate or other catalysts showed noticeable evidence of departure from a first-order course.

Table II shows the rate of the pyridine-catalyzed reactions at 52.9° of 2-pentyl chlorosulfite and a sample of 2-pentyl chlorosulfite in which 86% of the 1 and 3 hydrogens had been replaced by deuterium. The rates of the uncatalyzed reactions are calculated from the data of Boozer and Lewis.⁷

TABLE II
RATE OF CATALYZED DECOMPOSITION OF DEUTERATED AND UNDEUTERATED 2-PHENYL CHLOROSULFITES

Substituent	Catalyst concn. moles/l.	$k_{app} \times 10^4$, sec. ⁻¹	k_c , l./mole/sec.
H	0.0	0.928	
H	4.96×10^{-3}	6.83	0.119
D	0.0	0.616	
D	4.96×10^{-3}	5.65	.0951

Discussion

The increase in rate on adding the bases and their hydrochlorides shows that there is a real catalysis, and Fig. 1 shows that to a first approximation the rate increases linearly with the concentration of the catalyst. This approximation can be represented by equation 1

$$k_{app} = k_0 + k_c(C) \quad (1)$$

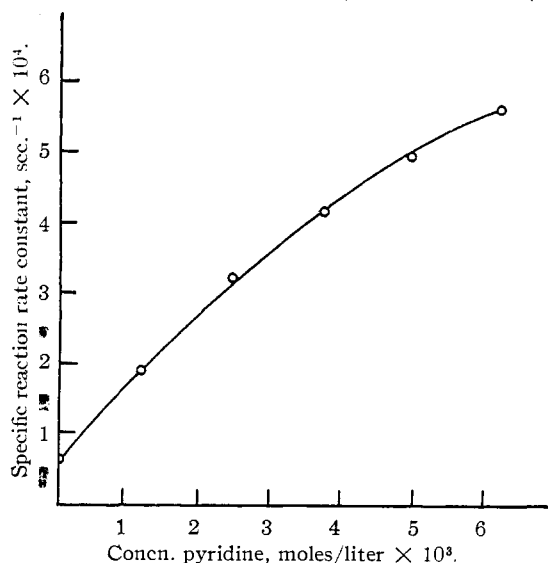


Fig. 1.—Dependence of apparent first-order rate constant k_{app} on pyridine concentration.

where k_0 is the constant for the uncatalyzed reaction and k_c is the second-order rate constant for the reaction of chlorosulfite with the catalyst of concentration (C). It is clear that the reaction studied is not a stoichiometric reaction of chlorosulfite with the amine, since the amount of amine is only of the order of 1% of that of the chlorosulfite. Table III shows the values of k_c calculated by this equation for the catalysts.

TABLE III
CATALYTIC CONSTANTS FOR VARIOUS BASES IN THE DECOMPOSITION OF ISOPROPYL CHLOROSULFITE

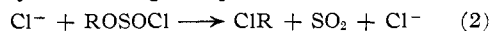
Catalyst	Concn., moles/l. $\times 10^3$	pK_a	k_c , l./mole ² ·sec.
Quinoline ^a	3.72	4.80 ^e	0.062
Lutidine ^a	3.72	6.58 ^d	.11
Dimethylaniline ^a	3.72	4.26 ^d	.036
Pyridine ^a	3.72	5.15 ^d	.095
Pyridine ^a	6.23		.080
Pyridine ^a	1.24		.099
Pyridine·CH ₃ Cl ^b	0.035		.30
Pyridine·C ₃ H ₇ Cl ^b	0.056		.30
Pyridine ^b	3.80		.021
Pyridine ^b	5.06		.020
Pyridine·HCl ^b	2.10		.027
Pyridine·HCl ^b	6.50		.023

^a At 52.9°. ^b At 39.8°. ^c Reference 13. ^d L. N. Ferguson, "Electron Structures of Organic Molecules," Prentice-Hall, Inc., New York, N. Y., 1952.

The lack of constancy of k_c with one catalyst corresponds to the curvature in Fig. 1 and hence the failure of eq. 1.

It is seen from Table I that pyridine and pyridine hydrochloride are equally effective catalysts. We attribute this to the conversion of the pyridine to its salt by the hydrogen chloride produced in an elimination reaction. The early stages of the reaction have not been followed with sufficient precision to allow a distinction between the established first-order elimination⁷ and an elimination produced by the pyridine. This distinction, which is in principle experimentally possible also by careful examination of olefin yield as a function of pyridine concentration, has not been attempted because of the difficulties connected with the high volatility of the olefin.

Of the various explanations of the catalytic effect, the most reasonable involves attack of chloride ion on the alkyl chlorosulfite, according to equation 2, somewhat analogous to the mechanisms proposed earlier¹⁰ on the basis of stereochemistry. One might expect that all second-order



rate constants for various sources of chloride ion would be the same under these circumstances, an expectation contrary to the results given in Table III. Here, the quaternary chlorides are more effective than the tertiary amines, which in turn vary among themselves. However, there is no reason to believe that the concentration of chloride ion is the same as the concentration of amine hydrochloride, and Table IV, giving the extinction coefficient of pyridine in the presence of hydrogen

chloride at the wave length of maximum absorption of the hydrochloride, shows that pyridine is not quantitatively converted to the conjugate acid in dioxane solution by hydrogen chloride, assuming that the ultraviolet absorption is sensitive to this alone. While pyridine has been reported to give a dihydrochloride,¹¹ this extra molecule of hydrogen chloride is most likely complexed with the chloride ion and not the light-absorbing positive ion of pyridine hydrochloride. If the amine hydrochloride is not completely ionized, one might expect to find a correlation between catalytic ability and base strength. The base strengths of the tertiary amines, as measured under rather different conditions do indeed show this correlation.

TABLE IV
CHANGE IN EXTINCTION COEFFICIENT OF PYRIDINE IN DIOXANE ON ADDING HYDROGEN CHLORIDE

(HCl)/pyridine	$\epsilon_{257, m\mu}$	(HCl)/pyridine	$\epsilon_{257, m\mu}$
0.0	2050	1.68	3580
1.25	3280	1.88	3630
1.36	3380	4.00	3720

Independent support for a mechanism involving chloride ion attack before ionization of the chlorosulfite is complete is given by the results with the deuterium substituted compound. A mechanism of this sort will clearly involve a transition state of lesser electron deficiency on carbon than one involving a carbonium ion intermediate, such as has been proposed for the uncatalyzed reaction.⁶ Thus the amount of hyperconjugation in the transition state should be less for the catalyzed reactions, and the retardation by β -deuterium substitution should be smaller.¹² As shown in Table II the ratio of catalytic constants for the undeuterated and deuterated compounds is 1.25, compared to the ratio 1.50 for the uncatalyzed reaction. The difference in activation energies for the two compounds is 0.15 kcal. This is also in agreement with the previously deduced statement that chloride ion is more able to satisfy the electron deficiency of a carbonium ion than is dioxane.⁶

An alternative mode of action of a base is to attack sulfur. The catalytic activity of pyridine hydrochloride does not absolutely disprove this mechanism, since we have already assumed that free pyridine may be present in a dioxane solution of the salt. The significant catalytic activity of the quaternary chlorides does suggest that free base is not necessary, and the activity of 2,6-lutidine is higher than one might expect for this mechanism since formation of a sulfur-nitrogen bond in this compound would probably be very unfavorable because of steric hindrance. This hindrance is for instance shown in the attack of the amines on the carbonyl group in the base-catalyzed hydrolysis of acetic anhydride where catalytic activity of 2,6-lutidine is far lower than one would predict from its base strength.¹³

One further explanation of the kinetic results is still open. Since ionization is a common reaction path for chlorosulfites, it is conceivable that the

(11) F. Kaufer and E. Kunz, *Ber.*, **42**, 385 (1909).

(12) E. S. Lewis and C. E. Boozer, *ibid.*, **76**, 791 (1954).

(13) V. Gold and E. Jefferson, *J. Chem. Soc.*, 1409 (1953).

(10) W. A. Cowdrey, E. D. Hughes, C. K. Ingold, S. Masterman and A. D. Scott, *J. Chem. Soc.*, 1267 (1937).

acceleration in rate on adding amine hydrochlorides is caused by an increase in rate constant of ionization resulting from an increase in ionic strength. The data with lithium perchlorate show that an accelerating effect is indeed present. Within the accuracy of the experiments, the small accelerating effect of the pyridinium perchlorate can be accounted for on the same basis. However, the effect seems too small to account for all the increase in rate observed with the amines, but the previous suggestion of an uncertainty of reaction order in the presence of lithium perchlorate weakens this argument. A more convincing piece of evidence comes from the investigation of the stereochemical result of the decomposition. A decomposition in the presence of 10^{-2} M lithium perchlorate gave 2-butyl chloride of predominantly retained configuration with 36% optical purity, and a 10^{-4} M solution yielded a chloride with 74% optical purity. This is to be contrasted with the more than 95% optical purity with retention in the absence of salts, and 67% optical purity with *inversion* in the presence of

10^{-8} M pyridine hydrochloride.⁶ Thus there must be a significant mechanistic difference between the action of lithium perchlorate and pyridine hydrochloride.

The racemization and possible change of kinetic order in the presence of lithium perchlorate are both consistent with the view that the ionic environment may promote ion-pair dissociation, giving therefore a symmetrically solvated carbonium ion.

The departure of the curve in Fig. 1 from linearity can also be attributed to a salt effect on both the second-order and first-order reactions. However, since the salt effects in such non-polar solvents are very complex, we have made no attempts to correct even k_0 for the salt concentration by using the lithium perchlorate data.

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HOUSTON, TEXAS

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

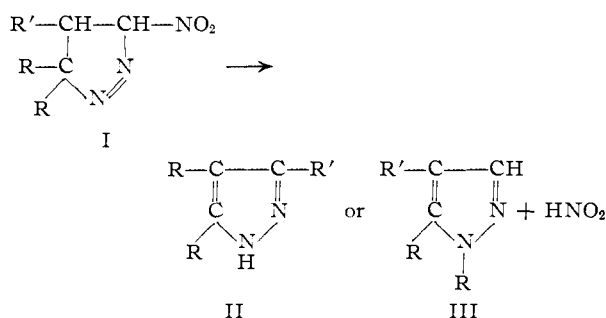
Reactions of Diazo Compounds with Nitroolefins. III. Group Migrations in the Decomposition of Nitropyrzazolines

BY WILLIAM E. PARHAM AND WILLIAM R. HASEK¹

RECEIVED AUGUST 21, 1953

A study of the reactions of certain nitroolefins with disubstituted diazo compounds, and subsequent decomposition of the resulting nitropyrzazolines has been made. Loss of nitrous acid from the nitropyrzazolines is accompanied by group migrations to carbon, resulting in the formation of 3,4,5-trisubstituted pyrazoles. The pyrazoles are postulated to arise from either a concerted twofold rearrangement of the Wagner-Meerwein type, or from a single migration from an abnormally orientated addition product.

In the preceding articles of this series the reaction of diazomethane and diazoacetic ester with nitroolefins was described,^{2,3} and mechanisms³ for the decomposition of 3-nitropyrzazolines by action of acids or bases into pyrazoles, by loss of the elements of nitrous acid, were discussed. As a result of this study, and in view of data available concerning rearrangements of the Wagner-Meerwein type, it was anticipated that the loss of nitrous acid from pyrazolines of type I would give, by migration of R groups, pyrazoles of type II or type III.



(1) Abstracted from the Ph.D. Thesis of William R. Hasek, University of Minnesota, 1953.

(2) W. E. Parham and J. L. Bleasdale, *THIS JOURNAL*, **72**, 3843 (1950).

(3) W. E. Parham and J. L. Bleasdale, *ibid.*, **73**, 4664 (1951).

A study of the reaction of diphenyldiazomethane with ω -nitrostyrene and 1-nitropropene, and the subsequent decomposition of the resulting nitropyrzazolines into pyrazoles constitutes the subject of this report.

When diphenyldiazomethane was allowed to react with ω -nitrostyrene, in the absence of solvent, a crystalline addition product was obtained in 41% yield. Although the structure of this product was not established with certainty, it was formulated as 3-nitro-4,5,5-triphenylpyrazoline (IV),⁴ instead of the isomeric pyrazoline V.

When the pyrazoline IV was treated with hydrochloric acid, oxides of nitrogen were liberated, and a product, melting at 265° and having the composition of a triphenylpyrazole, was obtained in quantitative yield. The structure of this pyrazole was established to be 3,4,5-triphenylpyrazole (VI) by its independent synthesis from benzaldesoxybenzoin

(4) Evidence was presented in the first paper of this series which established the structures of the nitropyrzazolines derived from the reaction of nitroolefins with diazomethane and diazoacetic ester. These products were analogous to pyrazolines of type IV. Furthermore, in the great number of cases where a diazo compound has been added to an activated olefin, the direction of addition is again that in which a nitrogen atom of the diazo group becomes attached to the α -carbon of the olefin. The only exception, reported by K. Von Auwers and O. Ungemach, *Ber.*, **66B**, 1205 (1933), is the formation of the two possible adducts from the reaction of ethyl phenylpropionate with ethyl diazoacetate.