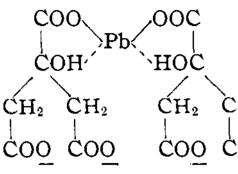
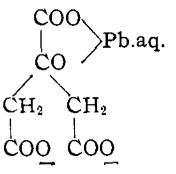
$[PbCi_2]^{4-}$:



$[PbCi']^{2-}$:



The coördination number of lead in the anion complex $[PbCi_2]^{4-}$ is four. Nothing certain can be said about the coördination number in the case of $[PbCi']^{2-}$. The latter may be hydrated.

3. **Conductometric Measurements.**—Figure 5 presents the composition and the results of three titrations. No change in conductivity (curve 1) occurs during the precipitation of $Pb_3Ci_2 \downarrow$. A break is obtained on the quantitative formation of the insoluble salt. A linear increase in conductivity occurs during the redissolving of the precipitate. In the reverse titration (curve 2) a break occurs at the point of complete precipitation of Pb_3Ci_2. Curve 3 is entirely different. It is composed of four branches with breaks between them. *The breaks lie at the calculated end-points of the formation of the various predicted compounds* (compare Table I). At the first break all the sodium hydroxide present in solution is used up for the quantitative formation of the soluble anion complex $[PbCi']^{1-}$. The free citrate remaining in solution reacts now with the lead, forming quantitatively the anion complex $[PbCi_2]^{4-}$ at the second break. On further addition of lead, the insoluble salts $Pb[PbCi']$ and $Pb_2[PbCi_2]$ are formed quantitatively at the third break.

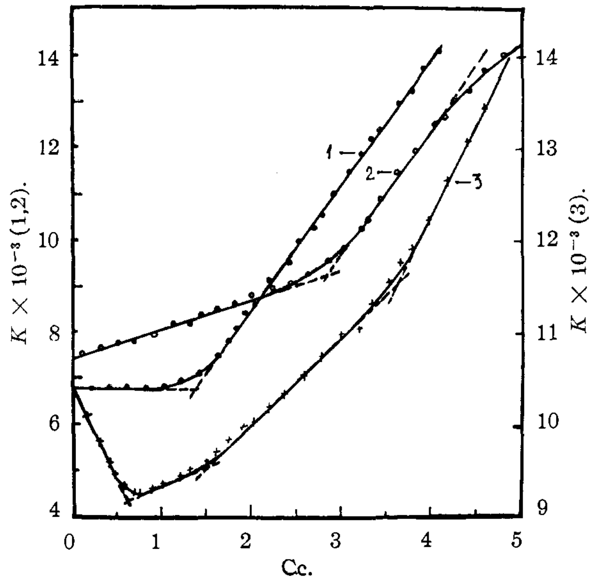


Fig. 5.—(1) 5 cc. 0.2 M $Pb(NO_3)_2$ + 45 cc. H_2O + x cc. 0.5 M Na_3Ci; (2) 5 cc. 0.2 M Na_3Ci + 45 cc. H_2O + x cc. 0.5 M $Pb(NO_3)_2$; (3) 4.5 cc. 0.25 M Na_3Ci + 3.75 cc. 0.1 M NaOH + 41.75 cc. H_2O + x cc. 0.5 M $Pb(NO_3)_2$.

JERUSALEM, ISRAEL

[CONTRIBUTION FROM THE MCPHERSON CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

Molecular Addition Compounds of Dinitrogen Tetroxide. II. Reactions with Tertiary Amines[1]

BY DEREK A. DAVENPORT, HAROLD J. BURKHARDT AND HARRY H. SISLER

RECEIVED APRIL 2, 1953

In ethereal solution at low temperatures, dinitrogen tetroxide reacts with tertiary amines to form yellow precipitates of the general formula $N_2O_4 \cdot 2B$, where B is pyridine, quinoline, isoquinoline, acridine, β-picoline, α-picoline or triethylamine. Addition compounds in which the mole per cent. of dinitrogen tetroxide is greater than that required by the formula $N_2O_4 \cdot 2B$ are also found with certain of these amines. All are unstable at room temperature. 2,6-Lutidine and 2-methylquinoline do not give addition compounds with dinitrogen tetroxide under the experimental conditions studied. The significance of these results is briefly discussed.

A recent communication[2] from this Laboratory reported the discovery of a new series of molecular addition compounds of dinitrogen tetroxide with a number of ethers. The results discussed in that communication indicated further that the compounds are true adducts of N_2O_4 molecules and do not contain NO_2 radicals or NO_2^+, NO_2^-, NO^+, NO_3^- ions. It was, therefore, of interest to us to see if similar compounds are formed with other Lewis bases, such as the tertiary amines, and, if so, to examine their properties.

Preliminary experiments showed that it would be necessary to carry out the reactions of dinitrogen tetroxide with tertiary amines in a solvent and at low temperatures in order to avoid oxidation–reduction or nitration reactions. Diethyl ether was used as a solvent and the reactions were run at about −75°. The addition compounds formed as insoluble, usually yellow, precipitates. The amines studied include pyridine, quinoline, isoquinoline, acridine, α-picoline, β-picoline, γ-picoline, 2,6-lutidine, 2-methylquinoline and triethylamine.

Reaction with Pyridine.—Pyridine combines with dinitrogen tetroxide, in ethereal solution at low temperatures, to yield a yellow precipitate. The results of a series of these reactions using various mole ratios of reactants are summarized in Table I, section a. Since, as discussed in the experimental section, the total weight of product could not be determined with a high degree of accuracy, the percentage figures listed in the last column of this table do not have a high degree of precision. This accounts for the total per cent. rising in a few cases

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[1] Presented at the March, 1953, Meeting of the Am. Chem. Soc. in Los Angeles.

[2] The first paper in this series: B. Rubin, H. Shechter and H. H. Sisler, THIS JOURNAL, **74**, 877 (1952).

to more than 100%. Figures given in the second column give the composition of the products.

TABLE I

THE REACTIONS OF TERTIARY AROMATIC AMINES WITH N_2O_4

	Amine	Mole ratio N_2O_4:amine in reactants	Mole ratio N_2O_4:amine in products	Fraction of wt. of sample represented by N_2O_4 and amine analyses, %
a	Pyridine	0.17:1	0.48:1	98.6
		0.87:1	.50:1	99.2
		1.08:1	.50:1	98.8
		2.14:1	.50:1	99.9
		3.24:1	.99:1	100.8
		5.71:1	1.46:1	103.0
		7.17:1	0.97:1	102.5
b	Quinoline	0.92:1[a]	.46:1	96.8
		1.02:1[b]	.50:1	100.1
		0.90:1[b]	.50:1	99.1
		0.69:1[b]	.50:1	99.8
c	Iso-quinoline	0.40:1[a]	.50:1	89.5
		0.57:1[a]	.49:1	90.4
		0.89:1[b]	.50:1	99.8
		1.17:1[b]	.50:1	98.2
d	α-Picoline	0.17:1	.50:1	...
		0.26:1	.67:1	100.1
		0.48:1	.82:1	99.6
		0.78:1	.86:1	101.3
		1.51:1	1.22:1	99.3
		4.15:1	1.33:1	99.3
e	β-Picoline	0.20:1	0.52:1	100.0
		0.35:1	0.85:1	98.3
		1.13:1	0.94:1	103.8
		4.44:1	1.38:1	101.1
		6.85:1	1.48:1	104.7

[a] Slow removal of solvent and excess reactant. [b] Rapid removal of solvent and excess reactant.

It is apparent from the results in Table I that a 1:2 addition compound of the empirical formula $N_2O_4\cdot 2C_5H_5N$ is readily formed even in the presence of a fourfold excess of dinitrogen tetroxide. With larger excesses of dinitrogen tetroxide, however, the compositions of the products are by no means so consistent. In some instances products approximating the composition of a 1:1 compound were obtained and in two experiments even higher N_2O_4 contents were indicated. It is not believed that the high contents of dinitrogen tetroxide were due to adsorbed dinitrogen tetroxide for the product was evacuated for five hours with a Hy-Vac pump at −10°, at which temperature the vapor pressure of dinitrogen tetroxide is quite high. All the addition products obtained with pyridine and dinitrogen tetroxide decompose fairly rapidly above 0°. Attempts were made to derive a reproducible technique for isolating a pure 1:1 compound of the formula, $N_2O_4\cdot C_5H_5N$. These attempts failed.

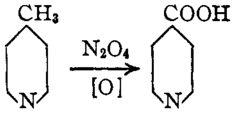
Reaction with Quinoline.—The reaction of quinoline with dinitrogen tetroxide yields a yellow precipitate of the composition $N_2O_4\cdot 2C_9H_7N$ even when a twofold excess of dinitrogen tetroxide is used. The results of a series of these reactions are given in Table I, section b. The compound $N_2O_4\cdot 2C_9H_7N$ decomposes at temperatures above about −25° and it is necessary to pump the excess reactant and solvent off rapidly to obtain the pure compound. (Note difference between the first run in Table I, section b, and the others in this section.) The substance visibly dissociates if it comes into contact with warm portions of the apparatus.

Reaction with Isoquinoline.—The reaction of isoquinoline with dinitrogen tetroxide in ethereal solution is very similar to that of quinoline, a yellow precipitate of the composition $N_2O_4\cdot 2C_9H_7N$ being obtained even in the presence of a twofold excess of dinitrogen tetroxide. The results of a series of these experiments are listed in Table I, section c. The compound $N_2O_4\cdot 2C_9H_7N$ decomposes above about −35° and must be separated rapidly from solvent and excess reactant to be obtained pure (note difference in analytical results between first two experiments and last two experiments in Table I, section c).

Reaction with Acridine.—Acridine reacts with dinitrogen tetroxide in ethereal solution to yield a yellow precipitate of the formula $N_2O_4\cdot 2C_{13}H_9N$. Two experiments in which five- and sixfold excesses of dinitrogen tetroxide were used resulted in the formation of this compound. *Anal.* Calcd. for $N_2O_4\cdot 2C_{13}H_9N$: N_2O_4, 20.4; Found: N_2O_4, 20.1, 19.9. Because of the low steam volatility of acridine it was not convenient to analyze for this component by our method. The compound $N_2O_4\cdot 2C_{13}H_9N$ appears to be somewhat more stable than the quinoline and isoquinoline compounds, but it decomposes fairly rapidly at room temperature.

Reaction with the Picolines.—The reactions of α- and β-picoline with dinitrogen tetroxide in ethereal solution proceed, as far as visual observation can detect, in much the same manner as in the case of the amines already discussed, except that the yellow product obtained with α-picoline exhibits a considerable degree of solubility in ether even at −78°. However, as the data in Table I, sections d and e, demonstrate, a product whose composition corresponds to the formula $N_2O_4\cdot 2C_6H_7N$ is obtained only in the presence of a considerable excess of amine. As the ratio of dinitrogen tetroxide to amine is increased in the reactants the proportion of dinitrogen tetroxide in the product increases and, at high N_2O_4/picoline ratios, products in which the N_2O_4/picoline ratio is considerably greater than 1:1 are obtained. For the same reason as given for the pyridine reaction, it is not believed that this is due to adsorbed dinitrogen tetroxide. Unsuccessful attempts were made with both α- and β-picolines by various washing and filtration techniques, to develop a method for preparing a pure 1:1 compound.

Dinitrogen tetroxide and γ-picoline also react to give a yellow precipitate, but the resulting product decomposes fairly rapidly even below −35°. Two approximate analyses of these yellow precipitates indicated that the behavior of γ-picoline with dinitrogen tetroxide is similar to that of the other picolines. If such a product has stood for any length of time and is diluted with water, a yellowish precipitate is obtained. This precipitate, on purification by sublimation *in vacuo*, yields a white, crystalline solid. The solid melts at 310–315° (uncor.) and is soluble in both acid and alkali. The amide of the substance was prepared and melted at 157°. These data show that the product is isonicotinic acid and that the γ-picoline has been oxidized by the dinitrogen tetroxide.



Reactions with 2-Methylquinoline and with 2,6-Lutidine.—When the reaction procedure described in the experimental section of this paper was carried out with 2-methylquinoline or with 2,6-lutidine (dimethylpyridine) no evidence of reaction was observed. When the solvent and dinitrogen tetroxide were pumped off the remaining product in each case consisted of from 98 to 100% of the original amine. We may thus conclude that these two amines do not form addition products with dinitrogen tetroxide under the conditions of our experiments. It is, of course, quite possible that a phase study might reveal such compounds.

Reaction with Triethylamine.—The reaction between triethylamine and dinitrogen tetroxide was carried out in the usual manner. The product first obtained in each experiment was a pink solid. As long as dinitrogen tetroxide is in excess the product remains pink; but as soon as excess triethylamine is added the pink product is converted to a yellowish brown substance. The pink solid twice exploded below 0° when the solvent had been removed. The yellow brown solid decomposes above 0°. The data for a series of representative experiments are summarized in Table II.

TABLE II

REACTION OF TRIETHYLAMINE WITH N_2O_4

Mole ratio N_2O_4:NEt_3 in reactants	Mole ratio N_2O_4:NEt_3	Color	Fraction of wt. of sample represented by N_2O_4 and NEt_3 analysis, %
0.38:1	0.48:1	Yellow-brown	94.4
.44:1	.47:1	Yellow-brown	92.3
.48:1	.50:1	Yellow-brown	92.7
.97:1	.54:1	Yellow-brown	85.6
2.23:1	1.18:1	Pink	89.4
4.74:1	1.38:1	Pink	86.5

It thus appears that the yellow-brown product is the 1:2 compound, *viz.* $N_2O_4\cdot 2N(Et)_3$, contaminated presumably with oxidation products of the triethylamine. The pink product corresponds to a higher ratio of dinitrogen tetroxide to amine.

Discussion

From the results reported above the following general conclusions may be drawn: (a) A number of tertiary amines combine with dinitrogen tetroxide to form solid addition compounds of the empirical formula $N_2O_4\cdot 2B$, (B = one molecule of amine). These include pyridine, quinoline, isoquinoline, acridine and triethylamine. In no case, even in the presence of large excesses of amine, is the mole per cent. of amine greater than that required by the formula, $N_2O_4\cdot 2B$.

(b) Certain other amines, notably the picolines, form addition compounds whose compositions approach that required by the formula $N_2O_4\cdot 2B$, only in the presence of large excesses of amine. Addition products of these substances having compositions varying from this extreme to compositions in which the dinitrogen tetroxide:amine ratio is actually greater than 1:1 are readily formed in the absence of a large excess of amine.

(c) Amines in which the basic nitrogen is highly hindered, *e.g.*, 2,6-lutidine and 2-methylquinoline do not form addition compounds with dinitrogen tetroxide under the conditions of our experiments.

In general, the nature of the addition compounds formed between dinitrogen tetroxide and tertiary amines seems to depend on steric factors, basicity of the amines, relative concentration of reactants and the susceptibility of the amine toward oxidation.

The importance of steric factors is shown by the fact that 2,6-lutidine and 2-methylquinoline give no isolable addition compounds. Furthermore the compound of dinitrogen tetroxide with α-picoline is much more soluble in diethyl ether than are compounds of the other heterocyclic amines studied. The results show that substitution in the α-position of the pyridine nucleus inhibits compound formation. A methyl group is a more effective inhibitor than an aromatic ring as acridine gives an addition compound whereas 2,6-lutidine does not. That an aromatic ring does have some effect in hindering compound formation is shown by the fact that α-picoline gives a compound (albeit a relatively soluble one) whereas 2-methylquinoline does not. Similar results were found by Arnold in the case of hindered aromatic ketones.[3]

Of the aromatic amines which have been shown by this work to produce addition compounds with dinitrogen tetroxide, the picolines are, as indicated by their aqueous dissociation constants, the most basic. They also exhibit the strongest tendency to form products containing less amine than that required by the formula $N_2O_4\cdot 2B$ or even by the formula $N_2O_4\cdot B$. This tendency is exhibited even in the presence of a considerable excess of amine. It is not possible at present to say whether there is a real relationship between this tendency and basicity or whether the correspondence is purely fortuitous.

The effect of oxidizability of the amine on the stability of the addition compounds is exemplified by the ease with which γ-picoline gives isonicotinic acid. The relative stability of the pyridine and acridine compounds is probably due to the stability of the amines toward oxidation.

Our experimental technique was to add the amine solution dropwise to the ethereal dinitrogen tetroxide solution and as a consequence the latter was always in excess at the beginning of a run. We must, therefore, assume the existence of equilibria of the type

$$N_2O_4\cdot 2B \rightleftarrows N_2O_4\cdot B + B$$

In the case of the picolines the equilibrium appears to lie toward the right whereas with the other het-

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[3] R. T. Arnold and P. N. Craig, THIS JOURNAL, **70**, 2791 (1948).

erocyclic amines it favors the left-hand side of this equation. That dinitrogen tetroxide may act as a bifunctional Lewis acid is seen from its compounds with the ethers, *e.g.*, $N_2O_4 \cdot 2Et_2O$.[2] It should be noted, however, that the compound $N_2O_4 \cdot 2Et_2O$ is almost certainly highly, if not completely, dissociated even at −35°, and that solvolytic reactions of the sort $N_2O_4 \cdot 2B + 2Et_2O \rightleftarrows N_2O_4 \cdot 2Et_2O + 2B$ are unimportant.

Experimental

Preparation of Materials.—Dinitrogen tetroxide for use in these studies was prepared and purified by methods previously described.[2]

Eastman Kodak Co. reagent grade diethyl ether was fractionated, dried over sodium and redistilled before use.

Pyridine, γ-picoline, isoquinoline, 2-methylquinoline and 2,6-lutidine were obtained from the Reilly Tar and Chemical Corporation. Quinoline, α-picoline, β-picoline and triethylamine were obtained from the Eastman Kodak Company. All these amines were dried for two weeks over barium oxide, carefully fractionated, retaining only a small middle fraction, and stored over barium oxide. They were all distilled afresh from barium oxide just before use. (The distillations in the case of quinoline and isoquinoline were under reduced pressure.) The purities of the amines were checked by comparison of boiling points with literature values and by titrating weighed samples of each amine against standard acid using a *p*H meter. These tests showed the amines to be quite pure.

Acridine obtained from the Eastman Kodak Company was recrystallized from aqueous alcohol. The recrystallized sample melted at 111° (lit. 110–111°).

Procedure.—The following technique was adopted. A cooled (−75°) ethereal solution of the amine was dropped from a jacketed dropping funnel into a cooled solution of dinitrogen tetroxide in ether, magnetically stirred, and maintained at −75°. The precipitated addition compounds were usually filtered and sometimes washed with fresh, cold ether if the amine were in excess. The solvent and excess reactant were pumped off under vacuum at a temperature of −10° or below. Since none of the resulting addition compounds is completely stable at room temperature, the weight of reaction product formed was found by allowing a known weight of water to be drawn (by vacuum) into the reaction flask, thus hydrolyzing the product. From the weight of the flask plus solution, the known weight of the empty flask plus the weight of the water, the weight of the product was calculated. Since this method involves taking a small difference between two large weights, it is of limited accuracy.

Analysis.—The aqueous solutions obtained by the above procedure were analyzed for amine by making the solution alkaline and by distilling the amine into an excess of standard acid followed by back titration using a *p*H meter. After removing the amine from a particular aliquot, Devarda's alloy was added to reduce the remaining nitrogen to ammonia, which was distilled into boric acid solution and titrated with standard acid using brom cresol green as indicator. Even if the weight of product is not known, or is known only approximately, this analysis will accurately indicate the formula if it is assumed that the product consists entirely of amine and dinitrogen tetroxide.

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COLUMBUS, OHIO

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Intermolecular Carbon Isotope Effect in the Decarboxylation of Normal Malonic Acid in Quinoline Solution[1]

BY PETER E. YANKWICH AND R. LINN BELFORD

RECEIVED APRIL 18, 1953

The intermolecular carbon isotope effect in the decarboxylation of isotopically normal malonic acid has been measured in quinoline solution in the range 34 to 118°. The complexity of the decomposition is such that neither the magnitudes nor the mode of temperature dependence of the results are in accord with predictions based on the simplified model suggested by Bigeleisen. It is concluded that the mechanism of the decarboxylation in quinoline involves at least one rapid, reversible equilibrium antecedent to the rate-determining step. The low entropy of activation for the reaction seems to require that the rate-determining step be a bimolecular process involving a molecule of solvent.

In a recent paper[2] we presented the results of experiments designed to yield the temperature coefficient of the intermolecular carbon isotope effect in the decarboxylation of malonic acid of normal isotopic constitution under conditions of homogeneous decomposition. The solvent chosen for those studies was 80% aqueous sulfuric acid. A plot of the isotope effect data obtained *vs.* $1/T$ was strongly curvilinear (*vide infra*) over the temperature range explored (56–129°), whereas a linear plot is predicted by calculations based on the corrected[3] simple model of Bigeleisen.[4] We did not offer an explanation of this apparent discrepancy, and further work to test the relation between theory and experiment seemed desirable.

In the present paper we present isotope effect results for malonic acid decarboxylation in quinoline. This solvent was chosen because studies of malonic acid decarboxylation in a variety of media[5,6] indicated that in quinoline the solute was highly solvated, and inappreciably ionized, resulting in a similar simplification of treatment of results as if the solute were not solvated at all.[7]

Experimental

Materials.—The malonic acid was the Eastman Kodak Co. white label grade. Preliminary tests showed that the purity of the material (99.9 ± 0.1% by acidimetric titration; m.p. 135°) was not increased significantly by recrys-

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(1) Presented before the Division of Physical and Inorganic Chemistry at the 123rd Meeting of the American Chemical Society, Los Angeles, California, March 15–19, 1953.

(2) P. E. Yankwich, R. L. Belford and G. Fraenkel, THIS JOURNAL, **75**, 832 (1953).

(3) J. Bigeleisen, *J. Phys. Chem.*, **56**, 823 (1952).

(4) (a) J. Bigeleisen, *J. Chem. Phys.*, **17**, 425 (1949); (b) J. Bigeleisen and L. Friedman, *ibid.*, **17**, 998 (1949).

(5) G. Fraenkel, R. L. Belford and P. E. Yankwich, in preparation.

(6) Y. Ogata and R. Oda, *Bull. Inst. Phys. Chem. Research* (*Tokyo*), *Chem. Ed.*, **23**, 217 (1944), made a related study.

(7) A study of these isotope effects for decomposition in a noncatalytic solvent is in progress in this Laboratory.