eutectic system. Thus, the 126° break corresponds to the potassium nitrate crystallographic transition and the 288° break corresponds to the eutectic temperature for the system.

The non-appearance of any evidence for the existence of $Ba(NO_3)_2 \cdot 2KNO_3$ above the eutectic temperature indicates that the double salt is stable only below the eutectic. Thus, the 201° break observed for the double salt must correspond to the decomposition into its simple component salts at the 10°/minute heating rate. It was found that the apparent decomposition temperature varied with the heating rate. At heating rates of 10, 8.5, 6.9, 5.6, 4.5, 3.2, 2.2 and 0.5°/minute, the corresponding decomposition temperatures were 201, 200, 198, 197, 196, 195, 194 and 187°, respectively. However, heating the double salt for 2 days at 168° brings about decomposition, whereas if it is maintained at 165° for 11 days the salt persists as determined by the presence or absence of this decomposition arrest in the heating curve. Hence, the true or equilibrium decomposition temperature lies between 165 and 168°. The thermal analysis gives a temperature which corresponds to a rapid rate of decomposition and not the true equilibrium temperature, a temperature at which the rate is evidently quite slow. This particular case is therefore another instance of the uncertainty of thermal analysis when applied to slow reactions.

Attempts at nucleation of the double salt with admixtures of up to 50 weight per cent. of the previously decomposed material or by rapid heating of the double salt to 195° and then cooling did not result in any change of the observed decomposition temperature. Rather the observed decomposition temperature was that characteristic of the heating rate.

Attempts at the thermal preparation of $Ba(NO_3)_2 \cdot 2KNO_3$ by the annealing of intimate stoichiometric mixtures of the component salts were not successful. Tempering such mixtures at 147° for 15 days or at 160° for 14 days did not yield any double salt as ascertained by thermal analysis.

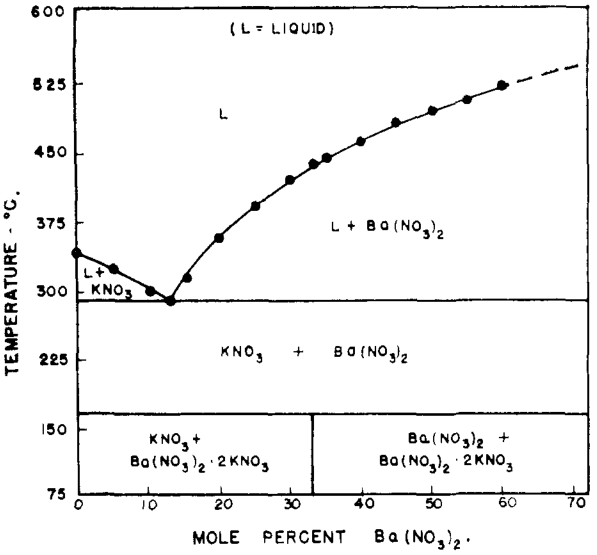

Fig. 1.—The system $Ba(NO_3)_2$–KNO_3.

The composite results obtained in the course of this investigation are given in Fig. 1.

The double salt, then, is a stable solid phase in the binary system up to about 168°, although it does not form at any measurable rate from the anhydrous salts even at temperatures just below this decomposition temperature. In the presence of water it forms very readily even at room temperature, and its range of existence as a stable solid phase in the aqueous system, making its appearance at about 168°, increases with falling temperature.

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The Stability of Silver(I) Complexes of Some 3- and 4-Substituted Pyridines[1]

BY R. KENT MURMANN[2] AND FRED BASOLO

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Pauling[3] has explained the greater stability of certain complexes of the transition elements compared to those of other metals on the basis of double bonding. He suggested that the transition elements can use for multiple bonding lower energy d orbital electrons which are not available to the non-transition elements. Although there is at present no direct proof of such double bonding in complexes, several experimental observations have been rationalized on this basis.[4] The stability constants of silver(I) complexes of some 3- and 4-substituted pyridines are reported here and the results obtained are also consistent with the concept of π-bonding.

Experimental

Pyridine, α-picoline, β-picoline and γ-picoline were redistilled over barium oxide and the middle portions used in these experiments. The physical constants of the amines are listed in Table I.

TABLE I

PHYSICAL CONSTANTS OF PYRIDINES

	B.p. or m.p., °C.
Pyridine	115.0–115.2
α-Picoline	127.5–128.0
β-Picoline	142.8–143.0
γ-Picoline	142.8–143.0
2-Methoxypyridine	142.5–143.0
3-Methoxypyridine	77–79 (15 mm.)
4-Methoxypyridine	72–73 (20 mm.)
Methyl picolinic ester	108–109 (22 mm.)
Methyl nicotinic ester	103–104 (20 mm.)
Methyl isonicotinic ester	100–102 (20 mm.)
Nicotinamide	M.p. 126–127
Isonicotinamide	M.p. 155–156
3-Cyanopyridine	M.p. 48–49
4-Cyanopyridine	M.p. 78–79

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(1) This investigation was supported by a grant-in-aid from the National Institutes of Health, Grant No. G-3239C2. Taken in part from a thesis submitted by R. Kent Murmann in partial fulfillment of the requirements for the Ph.D. degree, Northwestern University, 1954.

(2) University of Connecticut, Storrs, Connecticut.

(3) L. Pauling, "The Nature of the Chemical Bond," 2nd Ed., Cornell University Press, Ithaca, N. Y., 1948, p. 250.

(4) J. Chatt and R. A. Williams, *J. Chem. Soc.*, 3061 (1951); R. S. Nyholm and F. H. Burstall, *ibid.*, 3570, 3579 (1952).

2-Methoxypyridine was prepared from 2-bromopyridine by reaction with sodium methoxide dissolved in methyl alcohol.

3-Methoxypyridine was obtained through the reaction of 3-bromopyridine[5] with sodium methoxide in Carius tubes at 165° following the method of Meyer[6] for 3-ethoxypyridine.

4-Methoxypyridine was prepared in a manner analogous to that used by Hertog and Combe[7] for 4-ethoxypyridine.

The methyl esters of pyridine carboxylic acids were prepared by the method of Engler[8] and purified by distillation under reduced pressure.

The amides of pyridine carboxylic acids were obtained through the reaction of the esters with ammonia-saturated alcohol. Purification was accomplished by fractional precipitation of alcohol solutions with ether.

3-Cyanopyridine was obtained commercially and was crystallized from *o*-xylene–hexane mixtures until a constant melting point was obtained.

4-Cyanopyridine was produced in good yield by the dehydration of isonicotinic amide with phosphorus pentoxide. Purification was accomplished by crystallization with a mixture of *o*-xylene and hexane.

The acid dissociation constants of the substituted pyridines were determined by *p*H titration at low ionic strength using a glass electrode in conjunction with a calomel electrode which was protected with a saturated potassium nitrate salt bridge. A model G Beckman *p*H meter was used and the temperature of the solutions was maintained at 25 ± 0.1° with a constant temperature bath. The activity acid dissociation constants were then calculated using the activity coefficients obtained with the Debye–Hückel equation.

The activity formation constants of the silver(I) coordination compounds were determined by *p*H measurement of dilute solutions containing silver ion and the substituted pyridine. The method of Block and McIntyre[9] was used in the calculation of the formation constants.

For those amines which are very weak bases (*i.e.*, in the negatively substituted pyridines) it was impossible to compete the silver ion with hydrogen ion and obtain formation constants since the *p*H is not sensitive to the free amine concentration. In these cases the over-all activity formation constants were obtained by measurement of the e.m.f. given by cells of the type.

$$\mathrm{Ag(s)} \mid \mathrm{Ag^{+}M_{py}} \mid \mathrm{KNO_3(sat.)} \mid \mathrm{KCl(sat.)} \mid \mathrm{Hg_2Cl_2(sat.)} \mid \mathrm{Hg_2Cl_2(s)} \mid \mathrm{Hg(l)} \mid \mathrm{Pt(s)}$$

The validity of the assumptions made in calculating formation constants using these cells was confirmed by agreement of the over-all formation constants with pyridine obtained in this manner compared with those obtained by *p*H measurement.

TABLE II

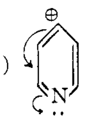
ACID DISSOCIATION AND SILVER(I) FORMATION CONSTANTS OF SUBSTITUTED PYRIDINES

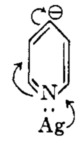
		pK_a[a]	log K_1[b]	log K_2[b]	log K_T[b]
1	Pyridine[c]	5.18	1.97	2.38	4.35[e]
2	β-Picoline[c]	5.52	2.00	2.35	4.35[e]
3	γ-Picoline[c]	6.08	2.03	2.36	4.39[e]
4	3-Methoxypyridine[c]	4.91	1.58	2.09	3.67
5	4-Methoxypyridine[c]	6.47	2.28	2.16	4.44
6	3-Cyanopyridine[d]	..	..	..	2.90
7	4-Cyanopyridine[d]	..	..	..	3.08
8	Nicotinamide[d]	..	..	..	3.22
9	Isonicotinamide[d]	..	..	..	3.01
10	Nicotinic acid methyl ester[d]	..	..	..	2.99
11	Isonicotinic acid methyl ester[d]	..	..	..	2.45

[a] Activity acid dissociation constants. [b] Silver(I) formation constants at 25.0°. [c] From *p*H measurements. [d] From e.m.f. measurements. [e] F. H. Verhoek and R. N. Bruehlman, THIS JOURNAL, **70**, 1401 (1948).

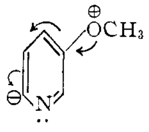
Results and Discussion

The results obtained are shown in Table II. Substitution of methyl and methoxy groups on the pyridine ring, as with compounds 2–5, is expected to increase the electron density in the ring. The fact that pyridine is a stronger base than either 3-methoxypyridine or 2-methoxypyridine (pK_a = 3.06) was not anticipated. Compounds 3, 4 and 5 form compounds with silver(I) ions which show a fairly good linear relationship between the stability of the complexes and the base strength of the pyridines. However, the pyridine complex is appreciably more stable than expected on the basis of its base strength alone as is likewise true to a lesser extent for the β-picoline complex. These results can be explained if one assumes that the contribution of d-orbital electrons enhances the stability of these compounds. In the case of pyridine there may be an appreciable tendency to accept electrons from the silver(I) ion because of the resonance structure (B), tending to reverse one of the resonance structures of pyridine (A).

(A) 

(B) 

The importance of such a resonance structure is minimized by the presence in the 4-position of either methyl or methoxy groups, which tend to place the negative charge on the nitrogen. Similarly, the π-bonding at the nitrogen for 3-methoxypyridine is negligible, perhaps due to the contribution of the resonance structure



This is not as important in β-picoline, which forms a stronger complex than expected on the basis of base strength, but not as strong as pyridine, where the extent of electron donation by silver(I) reaches a maximum in this series of complexes.

Compounds 6–11 contain electron-attracting groups and are expected to decrease the electron density in the pyridine ring. In fact these substances are all such weak bases that the pyridinium ions are largely dissociated in water and reliable values of pK_a were not obtained. In this series of compounds it should be noted that groups in the 4-position will tend to pull electrons from the silver(I) ion into the ring, or in other words increase the tendency to double bond. Groups in the 3-position cannot contribute to this type of resonance and the stabilities of these complexes are expected to largely correlate with the base strengths of the pyridines. It is of interest, therefore, that the cyanopyridine forms the least stable complex of those substituted in the 3-position whereas it is the most stable of the 4-substituted pyridine complexes. Since the cyano

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(5) S. M. McElvain and M. A. Goese, THIS JOURNAL, **65**, 2227 (1943).

(6) H. Meyer, *Monatsh.*, **26**, 1312 (1905).

(7) H. J. Hertog and F. Combe, *Rec. trav. chim.*, **70**, 586 (1951).

(8) R. Engler, *Ber.*, **27**, 1785 (1895).

(9) G. H. McIntyre and B. P. Block, THIS JOURNAL, **75**, 5667 (1953).

group is known[10] to have the greatest electron affinity, here again it would appear that this drain of electrons from the metal ion does contribute to the over-all stability of these complexes.

[10] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., New York, N. Y., 1940, p. 188.

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Remarks on a Cage Reaction*

BY A. REMBAUM AND M. SZWARC

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Frank and Rabinowitch[1] were the first to point out that molecules (or fragments) undergoing a bimolecular collision in a liquid medium are confined to a cage formed by the solvent molecules. This "cage effect" is responsible also for the recombination of fragments produced in a unimolecular dissociation process, and such a reaction should be distinguished from the ordinary bimolecular recombination. While the latter reaction takes place between "free" fragments which lost their identity, the cage recombination involves the two original fragments produced by the dissociation of a single molecule.

The cage recombination of acetate radicals has been investigated recently and the results are discussed in this note. Acetate radicals are produced by the unimolecular decomposition of acetyl peroxide (reaction 1)

$$(CH_3{\cdot}COO)_2 \longrightarrow 2CH_3{\cdot}CO_2 \qquad (1)$$

The decomposition of a dilute solution of this compound in isoöctane yields the following products only: methane, ethane, carbon dioxide and the products of disproportionation of isoöctyl radicals. The first and the last products result from reactions 2 and 3

$$CH_3{\cdot} + \text{iso-}C_8H_{18} \longrightarrow CH_4 + \text{iso-}C_8H_{17} \qquad (2)$$

$$2\text{iso-}C_8H_{17}{\cdot} \longrightarrow \text{disproportionation products} \qquad (3)$$

while the formation of ethane has been attributed[2] to a cage recombination of acetate radicals. Let us repeat briefly the facts which led to this conclusion.

The fraction of methyl radicals which appears as ethane is given by $2C_2H_6/CO_2$. Now, the latter ratio is 0.169 ± 0.014 (an average of 8 experiments) at 65°, but only 0.094 ± 0.018 (an average of 7 experiments) at 85°. These results were obtained by decomposing an approximately $5{\cdot}10^{-3}$ M solution of acetyl peroxide in isoöctane. The stationary concentration of radicals at 85° is, however, about 10 times higher than at 65°, since the rate of decomposition increases by a power of ten over this temperature range. Hence, the above results definitely exclude a bimolecular recombination of "free" methyl (or acetate) radicals as a source of ethane. On the other hand, the observed decrease in $2C_2H_6/CO_2$ with increasing temperature would be expected if the ethane results from a cage recombination, since the probability of a radical escaping from the cage increases with rising temperature.

Further evidence in favor of a cage reaction is provided by experiments carried out in the presence of quinone. Table I shows clearly that increasing the concentration of quinone in the solution decreases considerably the ratio CH_4/CO_2, leaving $2C_2H_6/CO_2$ essentially unchanged. Since the presence of quinone does not affect the rate of the unimolecular decomposition (measured by the rate of formation of CO_2), it is obvious that quinone reacts with "free" radicals, and that the ethane does not result from the recombination of such radicals. Similar results were obtained in isoöctane solution using iodine as a scavenger (see Table II).

TABLE I

$(Ac_2O_2) = 2.5.10^{-2}$ M in toluene soln., $T = 65°$.

Concn. quinone in toluene	C_2H_6/CO_2	CH_4/CO_2
None	0.12 (av. value)	0.74 (av.)
0.025	.12	.54
.050	.13	.37
.05	.15	.35
0.05	0.08	0.37
.1	.09	.25
.2	.09	.14
.2[a]	.08	.08

[a] 2,6-Dichloroquinone used instead of quinone.

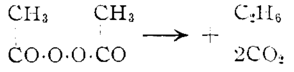
TABLE II

DECOMPOSITION OF DIACETYL PEROXIDE IN THE PRESENCE OF IODINE LIQUID PHASE

Acetyl peroxide in isoöctane $C = 5{\cdot}10^{-3}M$; $T = 85°$; decomp. ~ 60%.

Mole % of I_2	$2C_2H_6/CO_2$	CH_4/CO_2	$k \times 10^5$, sec.$^{-1}$
0.0	0.072	0.80	1.31
.1	.062	.010	1.25
.2	.062	.001	1.33

However, before one reaches the final conclusion that ethane *is* definitely formed in a cage reaction, one has to consider the possibility of two unimolecular modes of decomposition of acetyl peroxide which proceed simultaneously. One reaction (equation 1) leads to the rupture of the O–O bond and to the formation of radicals, while the second (equation 4) results from the $C{-}CH_3$ bond bending vibrations and yields ethane and two molecules of carbon dioxide in one step.



$$\begin{matrix} CH_3 & CH_3 \\ \vdots & \vdots \\ CO{\cdot}O & O{\cdot}CO \end{matrix} \longrightarrow \begin{matrix} C_2H_6 \\ + \\ 2CO_2 \end{matrix} \qquad (4)$$

If reaction 4 indeed takes place, its products should be observed in the liquid phase decomposition as well as in the gaseous decomposition. On the other hand, the products of the cage recombination cannot be observed in the gaseous decomposition, since this reaction is restricted to the liquid phase only. However, ethane is the main product of the gaseous decomposition, this product being formed by the recombination of methyl radicals.[3] Hence, in order to discriminate between these two alternatives: a cage reaction and reaction 4, we have carried out a series of experiments in which iodine vapor was

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* This investigation was supported by a grant from the National Science Foundation.

[1] N. H. Frank and E. Rabinowitch, *Trans. Faraday Soc.*, **30**, 120 (1934).

[2] M. Levy and M. Szwarc, THIS JOURNAL, **76**, 5981 (1954).

[3] A. Rembaum and M. Szwarc, *ibid.*, **76**, 5975 (1954).