

Kinetics and Mechanism of the Cyanoethylation of Alcohols

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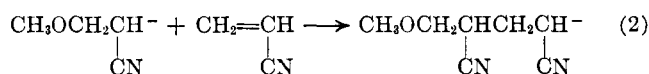
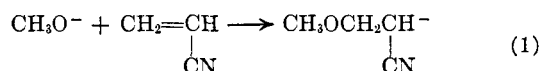
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The kinetics of the cyanoethylation of alcohols using lithium, sodium, and potassium alkoxide catalysts have been measured in the derived alcohol as solvent at various temperatures. The reaction is first order in acrylonitrile and alkoxide anion. The rate of reaction is independent of the alkali metal and increases with increase of the basic strength of the alkoxide anion as follows: isopropoxide > *n*-butoxide = *n*-propoxide > ethoxide > methoxide. It increases with decrease in the dielectric constant in methanol-dioxane mixtures. All this is in accordance with a mechanism involving a slow rate determining nucleophilic attack of alkoxide anion on acrylonitrile. The nucleophile is shown to be RO⁻ and not ROH.

In spite of the wide scope of the cyanoethylation reaction¹ only a few kinetic studies have been run on this subject. Ogata and Okano² made a kinetic study of the potassium hydroxide-catalyzed cyanoethylation of ethanolamine and acetylacetone in aqueous solution, and of the sodium methoxide-catalyzed cyanoethylation of methanol in methanol as solvent. The rate expressions obtained agreed with a mechanism involving a rate determining nucleophilic attack of the free amine, the carbanion, or the methoxide anion, on the β-carbon atom of the acrylonitrile. Oda and Shono³ studied the cyanoethylation of malonic ester and various esters of acetic acid in alkaline aqueous solution. Recently, Schmidt and Kubitzek,⁴ in a kinetic study of the cyanoethylation of some derivatives of malonic acid and malononitrile, using potassium *t*-butoxide as catalyst and dioxane-*t*-butyl alcohol (1:10) as solvent, found that the rate of reaction is first order in acrylonitrile.

In the present investigation the rates of reaction of several alcohols with acrylonitrile—using lithium, sodium, and potassium alkoxides as basic catalysts—have been measured at several temperatures, to confirm the mechanism from the kinetic standpoint as well as to identify the attacking species. Apart from its intrinsic interest, this class of reaction is of importance in its relation to the alkoxide-initiated anionic polymerization⁵ and graft polymerization of acrylonitrile,⁶ which is currently being investigated in our laboratory and was found to proceed by the following steps:



Reaction 1 is common to both polymerization (initiation) and cyanoethylation.

Results

The kinetic data for the cyanoethylation of methanol in the presence of lithium methoxide and sodium methoxide as basic catalysts in absolute methanol are summarized in Table I.

The rate of cyanoethylation of methanol was apparently first order in the concentrations of both acrylo-

TABLE I
RATES OF CYANOETHYLATION OF METHANOL IN METHANOL, AT 25°

CH ₂ =CH—CN, mole/l.	10 ² [CH ₃ OMe] (Me=Li, Na), mole/l.	10 ³ k ₁ , min. ⁻¹	k ₂ , ^a l./mole- min.
0.304 CH ₃ OLi	4.040	23.870	0.591
0.506	4.040	24.720	0.612
1.013	4.040	28.840	0.714
1.519	4.040	30.100	0.745
0.506 CH ₃ ONa	0.400	2.397	0.599
0.506	1.373	8.625	0.628
0.506	2.747	17.940	0.653
0.506 ^b	4.120	28.973	0.703
0.506	7.920	63.064	0.865
0.506	13.200	99.319	0.725

^a Average value of k₂ with lithium methoxide catalyst is 0.666 ± 0.064 l./mole min., with sodium methoxide catalyst 0.722 ± 0.087 l./mole min. ^b Cyanoethylation of methacrylonitrile was carried out under the same conditions.

nitrile and the catalytic methoxide anion. Since the methoxide concentration remained constant in any given run, we fitted the raw data with the equation:

$$k_2 t = \frac{2.303}{b} \log \frac{a}{a-x} \quad (3)$$

where k₂ = second order rate constant defined by equation 3, a = initial concentration of acrylonitrile, b = concentration of alkali metal alkoxide, (a-x) = concentration of acrylonitrile at time t. Plots of log a/(a-x) vs. t at any given temperature gave straight lines (Fig. 1), from the mean slope of which first-order rate constants were calculated. The second-order rate constant k₂ was calculated by means of the equation k₁ = k₂[RO⁻], where RO⁻ is the alkoxide anion. The rates of cyanoethylation, calculated from the initial slopes of conversion vs. time plots, increased linearly with both concentrations of acrylonitrile and methoxide anion.

The effect of the alkali metal on the rate of cyanoethylation was studied under comparable conditions in methanol as solvent at various temperatures—using lithium, sodium, and potassium methoxides as basic catalysts. The results given in Table II show that at a given temperature the same rate of cyanoethylation is obtained with lithium, sodium or potassium methoxide catalysts (Fig. 2). Accordingly, the energy of activation was also the same for the cyanoethylation of methanol in the presence of these methoxides—18.7 kcal/mole. The entropy of activation as calculated from the absolute rate theory⁷ was -7.2 e.u.

(7) W. F. K. Wynne-Jones and H. Eyring, *J. Chem. Phys.*, **32**, 492 (1935); S. Glasstone, K. J. Laidler, and H. Eyring, "Theory of Rate Processes," McGraw Hill, New York, N. Y., 1941, p. 196.

(1) H. A. Bruson, *Org. Reactions*, **V**, 79 (1949).

(2) Y. Ogata and M. Okano, *J. Am. Chem. Soc.*, **78**, 5426 (1956).

(3) R. Oda and T. Shono, *J. Chem. Soc. (Japan)*, **78**, 1683 (1957).

(4) U. Schmidt and H. Kubitzek, *Ber.*, **93**, 866 (1960).

(5) A. Zilkha, B.-A. Feit, and M. Frankel, *J. Chem. Soc.*, 928 (1959);

A. Zilkha and B.-A. Feit, *J. Appl. Polymer Sci.*, **5**, 251 (1961).

(6) A. Zilkha, B.-A. Feit, and A. Bar-Nun, Israel patent 15,962 (August 30, 1961).

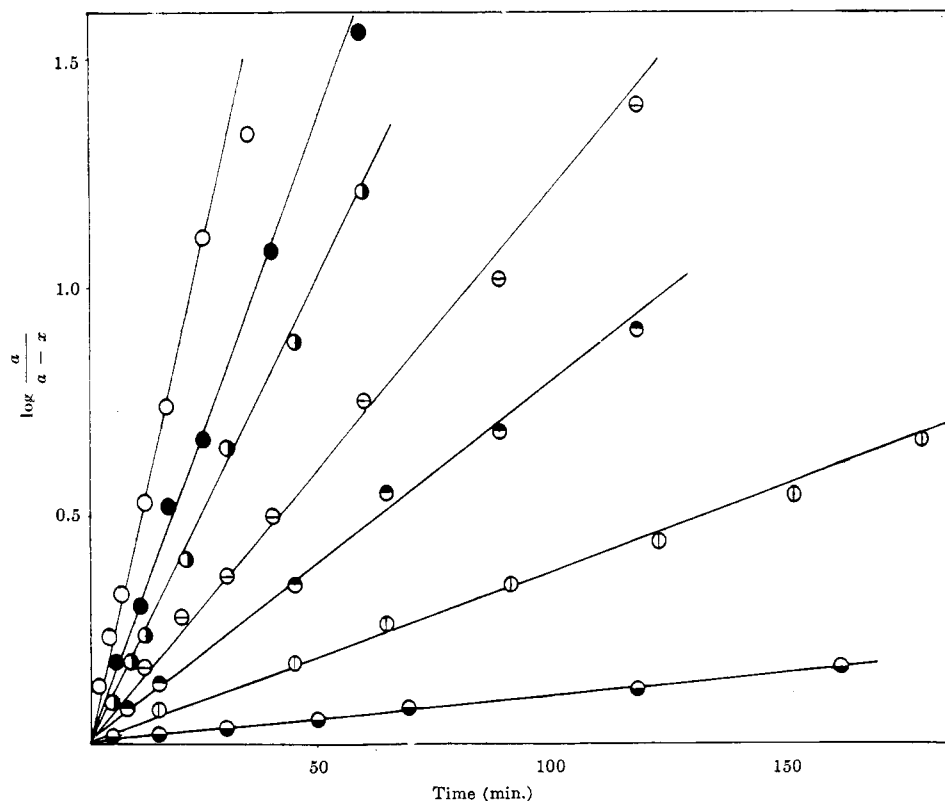


Fig. 1.—Rate of cyanoethylation of methanol in the presence of CH_3ONa at 25°C . 10^2 (CH_3ONa), mole/l.: \ominus 0.400, \oplus 1.373, \bullet 2.749, \ominus 4.120, \circ 5.493, \bullet 7.920, \circ 13,200

TABLE II

RATE OF CYANOETHYLATION OF METHANOL IN THE PRESENCE OF LITHIUM, SODIUM, AND POTASSIUM METHOXIDES

Temperature, $^\circ\text{C}$.	Alkali methoxide	10^2 [Methoxide] mole/l.	10^2k_1 , min. $^{-1}$	$10k_2$, l./mole min.
0	CH_3OLi	4.040	1.545	0.382
0	CH_3ONa	4.092	1.928	0.471
0	CH_3OK	3.670	1.394	0.380
15	CH_3OLi	4.036	7.931	1.965
15	CH_3ONa	4.092	9.612	2.349
15	CH_3OK	4.040	8.551	2.117
20	CH_3OLi	4.040	15.505	3.838
25	CH_3OLi	4.040	24.720	6.120
25	CH_3ONa	4.120	28.973	7.032
25	CH_3OK	4.400	25.836	6.395

TABLE III

EFFECT OF RO^- ON THE RATE OF CYANOETHYLATION OF THE DERIVED ALCOHOL AT 20°C ^a

Alkoxide	10^3k_1 , min. $^{-1}$	k_2 , l./mole min.
Methoxide	2.309	0.348
Ethoxide	20.909	3.151
<i>n</i> -Propoxide	38.333	5.749
<i>n</i> -Butoxide	38.333	5.749
Isopropoxide	115.000	17.249

^a Experimental conditions: initial concentration of acrylonitrile, 0.506 mole/l.; concentration of potassium alkoxide, 6.667×10^{-3} mole/l.

The effect of the basic strength of the alkoxide anion RO^- on the rate of cyanoethylation of the parent alcohol was studied to measure the relative reactivity of the alcohols in this reaction, as well as to establish the exact character of the nucleophile attacking the double bond of the acrylonitrile. This was investigated using potassium alkoxides as basic catalysts, since the solu-

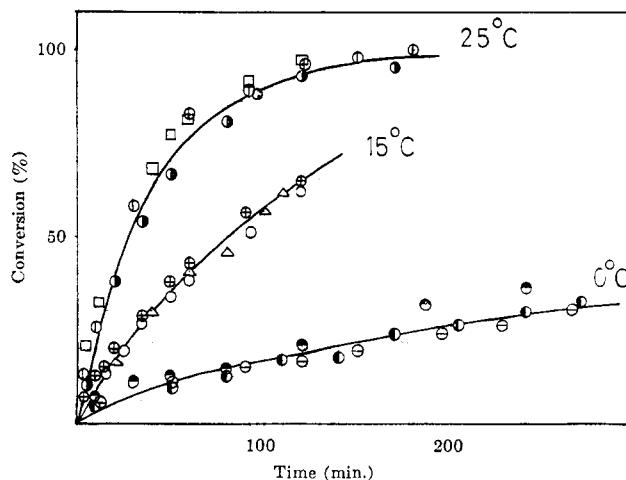
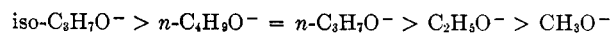


Fig. 2.—Rates of cyanoethylation of methanol in the presence of CH_3OLi , CH_3ONa , and CH_3OK . CH_3OLi : \bullet , \circ , \circ ; CH_3Na : \ominus , \oplus , \square ; CH_3OK : \ominus , Δ , \circ

bilities of the corresponding lithium and sodium alkoxides of the higher alcohols were limited. The results are summarized in Table III. In all cases the reaction was first order in acrylonitrile (Fig. 3) and good reproducibility was obtained. The rate of cyanoethylation increased with increase of the basic strength of the alkoxide anion as follows:



This order of reactivity is in accordance with the decreasing order of acidity of the derived alcohols as determined by Norris and Cortese⁸ from the relative second-order rate constants of the reaction between the alcohols and *p*-nitrobenzoyl chloride.

(8) J. F. Norris and F. Cortese, *J. Am. Chem. Soc.*, **49**, 2640 (1927).

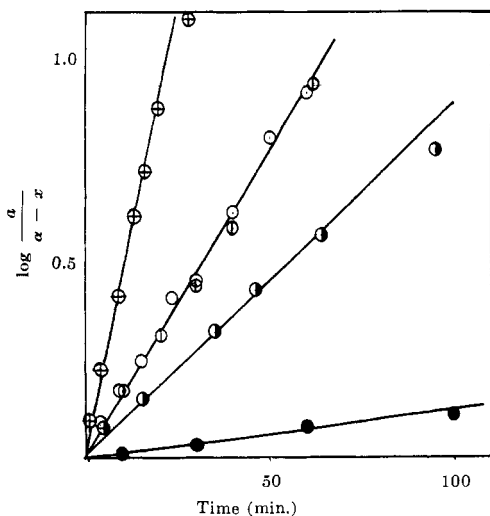


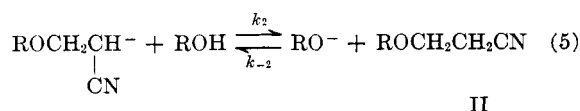
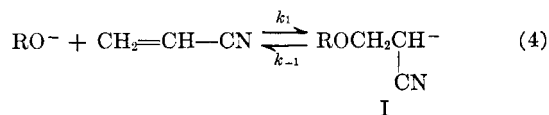
Fig. 3.—Effect of RO^- on the rate of cyanoethylation.
 ● CH_3OK ; ○ $\text{C}_2\text{H}_5\text{OK}$; ○ $n\text{-C}_3\text{H}_7\text{OK}$; ○ $n\text{-C}_4\text{H}_9\text{OK}$; ○ $i\text{-C}_3\text{H}_7\text{OK}$

Normally, the rate of reaction between an ion and a neutral molecule should be somewhat faster in a medium which has the lower dielectric constant.⁹ Rates of cyanoethylation of methanol using potassium methoxide catalyst were measured in different methanol-dioxane mixtures as solvent. Increase in per cent dioxane (dielectric constant 2) decreases the dielectric constant of the reaction mixture. With increase of per cent dioxane from 0 up to 50, there was a fourfold increase in the rate of cyanoethylation (Table IV). The rate of reaction was first order in acrylonitrile.

Methacrylonitrile was compared to acrylonitrile as regards the rate of addition of methanol to the double bond. Under comparable conditions (Table I) only 4–6% of the methacrylonitrile reacted after 180 minutes in the presence of sodium methoxide, whereas 90% of acrylonitrile reacted after 90 minutes using lithium methoxide as basic catalyst.

Discussion

The available data are consistent with a mechanism involving a slow addition of alkoxide anion to acrylonitrile, followed by a rapid abstraction of a proton from the solvent by the carbanion intermediate, as follows:



Steady-state treatment of equations 4 and 5 gives expression 6 for the rate of reaction:

$$R = -\frac{d[\text{AN}]}{dt} = \frac{[\text{RO}^-](k_1k_2[\text{AN}][\text{ROH}] - k_{-1}k_{-2}[\text{II}])}{k_{-1} + k_2[\text{ROH}]} \quad (6)$$

$k_2 \gg k_{-2}$ since ROH is a stronger acid than II ($\text{p}K_a$ of methanol 16.7¹⁰ and of acetonitrile 25¹¹); in the kinetic

rate measurements the yields of the cyanoethylation products were mostly quantitative, thus $k_1 \gg k_{-1}$; also the concentration of the alcohol which is present in great excess can be regarded as constant. Following these assumptions, equation 6 then becomes

$$R = k'[\text{AN}][\text{RO}^-] \quad (7)$$

where

$$k' = k_1 / \left(\frac{k_{-1}}{k_2[\text{ROH}]} + 1 \right)$$

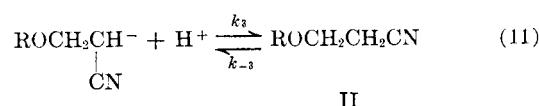
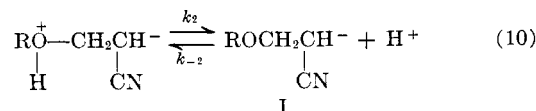
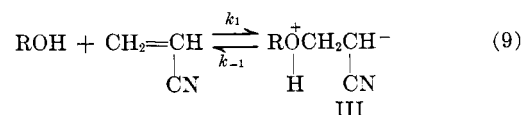
Since $k_{-1}/k_2[\text{ROH}] \ll 1$ it follows that $k' \simeq k_1$ and the final rate equation is

$$R = k_1[\text{AN}][\text{RO}^-] \quad (8)$$

This is a second-order rate equation—first order in each acrylonitrile and the alkoxide anion. The second-order rate constant of this rate equation is k_1 , which means that step 4, which is the nucleophilic attack of the free alkoxide anion RO^- on the β -carbon atom of the acrylonitrile, is the slow rate determining step, while the protonation of the intermediate carbanion (I) is the rapid one. The second-order rate constant obtained in the present work for the cyanoethylation of methanol at 25° is approximately the same as that obtained previously under similar conditions.²

In the above cited kinetic studies on cyanoethylation reactions, in investigations of various Michael-type addition reactions¹² and of other similar reactions such as addition of alcohols and mercaptans to ethylene oxide,^{13,14} it was also concluded that the first and rate determining step was a nucleophilic attack of the conjugate base of the active hydrogen compound, on the activated double bond.

There exists the possibility that the nucleophile is the alcohol itself and not the alkoxide anion. A mechanism of this sort has been suggested¹⁵ for the kinetically studied hydrolysis of benzylidene malononitrile in 95% ethanol, where it was found that the nucleophilic attack on the double bond was by water, and not by hydroxide or ethoxide ions present in the reaction mixture. In our case, such a mechanism requires the addition of alcohol to the double bond of acrylonitrile to give the oxonium ion-anion (III). This is followed by loss of a proton from the positive oxygen to give the carbanion (I) which is then protonated by the solvent, as follows:



(12) M. J. Kalmet and D. J. Glover, *ibid.*, **78**, 4556 (1956); T. Hine and L. A. Kaplan, *ibid.*, **82**, 2915 (1960).

(13) G. Gee, W. C. E. Higginson, P. Levesley, and K. J. Taylor, *J. Chem. Soc.*, 1338 (1959); G. Gee, W. C. E. Higginson, and G. T. Merrall, *ibid.*, 1345 (1959).

(14) J. P. Danehy and C. J. Noel, *J. Am. Chem. Soc.*, **82**, 2511 (1960).

(15) S. Patai and Z. Rappoport, *J. Chem. Soc.*, 383 (1962).

(9) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1960, p. 135.

(10) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," G. Bell & Sons Ltd., London, 1953, p. 726.

(11) R. G. Pearson and R. L. Dillon, *J. Am. Chem. Soc.*, **75**, 2439 (1953).

Deriving a rate equation, based on this reaction scheme, assuming steady-state conditions gives:

$$R = \frac{k_1 k_2 k_3 [\text{ROH}][\text{AN}] - k_{-1} k_{-2} k_{-3} [\text{II}]}{k_2 k_3 + k_{-1} k_3 + k_{-1} k_{-2}} \quad (12)$$

It is obvious that $k_2 \gg k_{-1}$, $k_3 \gg k_{-2}$, and $k_3 \gg k_{-3}$; also the concentration of the product II may be neglected, since the rates measured were initial rates. Thus equation 12 is reduced to:

$$R = k_1 [\text{ROH}][\text{AN}] \quad (13)$$

Since the concentration of the solvent ROH may be regarded constant it follows that

$$R = k' [\text{AN}] \quad (14)$$

According to equation 14 there should be no dependence of the reaction rate on the alkoxide concentration. This is contrary to the experimental results and to the over-all second-order rate constant observed, so that the possibility of the alcohol being the nucleophile is excluded.

If the alkoxide anion were acting as an ion pair and not as a free anion, differences in the rate of reaction might be expected depending on the different ionic character of the ion pairs RO^-Li^+ , RO^-Na^+ , and RO^-K^+ . The experimental results for the cyanoethylation of methanol show that the rate of reaction is the same when lithium, sodium, or potassium methoxides are used as basic catalysts (Table II). It may therefore be concluded that the nucleophile is the free alkoxide anion, and also that the three alkali metal methoxides are completely dissociated into ions under the investigated conditions. It is worthwhile to note that the nucleophilic reactivity of the ion pair $\text{CH}_3\text{O}^-\text{Na}^+$ in the addition of methanol to ethylene oxide, is tenfold smaller than that of the methoxide anion.¹³

As shown, the addition of RO^- to the double bond of acrylonitrile is the slow rate determining step. It is also well known that the rate of nucleophilic additions and substitutions increases with increase of the basic strength of the nucleophile.¹⁶ The observed increase in the rate of cyanoethylation with increase of the basic strength of the RO^- anion (Table III) is in accordance with these facts. Indeed, there is a linear dependence between the rate of cyanoethylation and the relative acidity⁸ of the added alcohols (Fig. 4). In a kinetic study of the closely similar reaction, that of the addition of alcohols to methyl vinyl ketone in alcoholic solvents, using the derived alkali metal alkoxides as basic catalysts, Ferry and McQuillin¹⁷ also found that the rate of reaction increased with the alcohol ROH in the following order: $\text{R} = \text{iso-C}_3\text{H}_7 > \text{C}_2\text{H}_5 > \text{CH}_3$.

The increased rate of cyanoethylation in methanol-dioxane mixtures, with decrease of the dielectric constant (Table IV) also suggests that the rate determining step is a reaction between an ion and a neutral molecule.⁹ It might therefore be that the increase of rate of cyanoethylation with the different alcohols (Table III) is also partially due to lowering in the dielectric constant of the alcohols. However, it can be seen that the rate increase with the different alcohols is much more than that required by the lowering in the dielectric constant, a fact which is also clearly seen from the results obtained with *n*-butyl alcohol and isopropyl

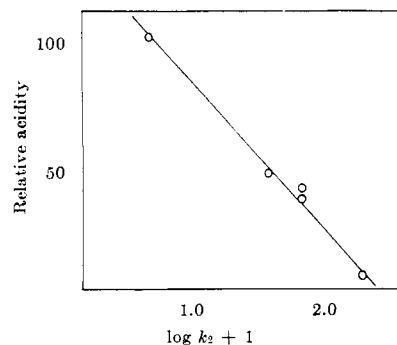


Fig. 4.—Dependence of rate of cyanoethylation on the acidity of the alcohol. Relative acidities of the alcohols⁸: methanol (100), ethanol (45.7), *n*-butyl alcohol (40.7), *n*-propyl alcohol (35.9), isopropyl alcohol (5.4).

TABLE IV
RATES OF CYANOETHYLATION OF METHANOL IN METHANOL-DIOXANE SOLVENT AT 20°^a

Dioxane, % by volume	$10^3 k_1$, min. ⁻¹	k_2 , l./mole- min.
0	2.309	0.348
20	3.565	0.535
33	5.111	0.767
50	8.415	1.262

^a Experimental conditions: initial concentration of acrylonitrile, 0.506 mole/l.; concentration of potassium alkoxide, 6.667×10^{-3} mole/l.

alcohol which have comparable dielectric constants (17.1 and 18.3, respectively,¹⁸ at 25°). It may therefore be concluded that the basic strength of the alkoxide anion is the main factor affecting the rate of the cyanoethylation.

Experimental

Materials.—Acrylonitrile (B.D.H.) was purified according to the method of Bamford and Jenkins.¹⁹ Absolute methanol (B.D.H.) for anhydrous titrations containing no more than 0.01% water was used. Absolute ethanol (99%) was dried over magnesium and distilled. *n*-Propyl alcohol was dried over magnesium. *n*-Butyl alcohol was distilled over sodium and further dried by sodium and di-*n*-butyl phthalate. Isopropyl alcohol was first dried over calcium sulfate and then over calcium metal and distilled. Dioxane was purified and dried according to Vogel.²⁰ All these materials were kept under nitrogen in flasks fitted with self sealing rubber caps.

Alcoholic alkoxide solutions were prepared by dissolving the alkali metal in the respective alcohol under reflux; care was taken to avoid moisture. The alcoholic alkoxide solutions were kept in brown bottles. They must be fresh, as they tend to become colored and decompose. Methoxide solutions were the most stable. The concentration of the catalyst solution was determined by titration of an aliquot portion with standard acid using phenolphthalein as indicator.

Procedure for Kinetic Measurements.—All glass apparatus was dried in an oven at 120° and transferred to a vacuum desiccator containing phosphorus pentoxide to cool. Immediately before use the apparatus was quickly assembled and flushed with dry oxygen-free nitrogen. The reaction was carried out in a 250-ml. three-necked flask, fitted with a self sealing rubber cap through which the reagents were added by syringes, an inlet for nitrogen and a capillary tube fitted with a stopcock which served as an outlet for removing aliquot portions by applying positive

(16) Ref. 10, p. 694.

(17) N. Ferry and F. J. McQuillin, *J. Chem. Soc.*, 103 (1962).

(18) "Handbook of Chemistry and Physics," 41st ed., Chem. Rubber Publishing Co., Cleveland, Ohio, 1959-1960, p. 2517.

(19) C. H. Bamford and A. D. Jenkins, *Proc. Roy. Soc. (London)*, **A 216**, 515 (1953).

(20) A. I. Vogel, "Practical Organic Chemistry," 3rd ed., Longmans Green & Co., London, 1957, p. 177.

nitrogen pressure. The flask was placed in a constant temperature water bath, where the temperature was controlled to $\pm 0.05^\circ$. Acrylonitrile, solvent, and alkoxide solutions were transferred to the reaction flask by syringes, filled under positive nitrogen pressure. The solution of acrylonitrile in alcohol was brought to the required temperature, and catalyst solution was then added. Aliquot portions were removed at various time intervals, into 50-ml. weighed volumetric flasks containing 5 ml. of solution of hydrochloric acid in isopropyl alcohol (1 *M*).

Acrylonitrile was determined volumetrically by the *n*-dodecyl mercaptan method.²¹

Acknowledgment.—The authors are pleased to acknowledge partial support of this work by the Israel National Council for Research and Development.

(21) American Cyanamid Company, "The Chemistry of Acrylonitrile," 1951, p. 69.

Anionic Oxidation of Heterocyclic Nitrogen Bases and the Effect of Solvent on Such Reactions^{1a}

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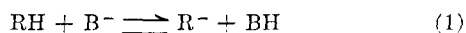
Process Research Division, Esso Research & Engineering Company, Linden, New Jersey

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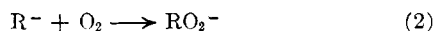
Pyrrole and the three picoline isomers were autoxidized in solutions of strong bases near ambient temperature. Since the oxidation does not take place at measurable rates without base being present, the carbanions formed from these compounds must be attacked by oxygen. Pyrrole is readily oxidized in potassium *t*-butoxide-*t*-butyl alcohol as the base-solvent medium. Complex products are formed in this oxidation which has an apparent energy of activation of 4 kcal./mole. All three picoline isomers are oxidized with practically quantitative selectivity to the potassium salts of the corresponding carboxylic acids using the same base, potassium *t*-butoxide, but changing the solvent to *N,N*-dimethylformamide. The direct addition of oxygen to the picoline carbanions is proposed as the mechanism accounting for these oxidations.

Molecular oxygen reacts readily with a number of organic compounds in solutions of strong bases, even under mild conditions where the thermal reaction is immeasurably slow in the absence of base. Experimental evidence^{1b-5} indicates that these reactions involve the oxidation of anionic species, since only compounds containing relatively acidic hydrogen atoms have been reported to undergo such oxidations. Thus oxygen molecules react with carbanions formed by abstracting a proton from the acidic carbon-hydrogen bonds of compounds such as 2-nitropropane,² substituted fluorenes,⁴ and *p*-nitrotoluene.⁵

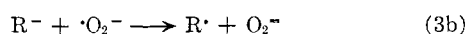
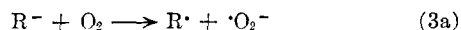
The various mechanisms postulated for the attack of oxygen molecules on carbanions have been reviewed recently by Russell and Moye.⁵ According to these reaction schemes, following anion formation *via*



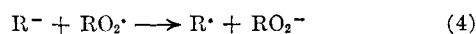
oxygen may add directly to form the anion of a hydroperoxide^{1,4}



or the anion may exchange electrons with oxygen⁵:



Finally, an electron-exchange reaction with thermally formed peroxy free radicals has been suggested to explain the anionic oxidation of 2-nitropropane²:



Reaction 4 would then lead to a chain reaction sequence *via*

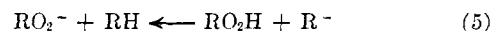
(1)(a) Paper presented at 141st National Meeting of the American Chemical Society, Washington, D. C., March, 1962; (b) W. E. Doering and R. M. Haines, *J. Am. Chem. Soc.*, **76**, 482 (1954).

(2) G. A. Russell, *ibid.*, **76**, 1595 (1954).

(3) C. Walling, "Free Radicals In Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, pp. 464-465.

(4) Y. Sprinzak, *J. Am. Chem. Soc.*, **80**, 5449 (1958).

(5) G. A. Russell and A. J. Moye, 137th National Meeting of the American Chemical Society, Division of Petroleum Chemistry Preprints, **5**, C-25, Cleveland, Ohio, 1960.



According to Russell and Moye, the free radicals formed in step 3 may dimerize or react further with oxygen, depending on the "availability" of oxygen in the system.

The present study reports on the anionic oxidation of heterocyclic nitrogen compounds—pyrrole and the three isomeric picolines. Both pyrrole and pyridine derivatives occur in petroleum oils and are representative of the "nonbasic" and "basic" nitrogen compound types, respectively.⁶ While the nitrogen-hydrogen bond of the pyrrole molecule is quite acidic, and therefore proton abstraction may be expected to occur with relative ease, the hydrogen atoms of the methyl groups of the picolines are considerably less acidic so that the latter compounds are likely to be inert under similar conditions of base, solvent, and temperature.

Experimental

Materials.—The oxidation experiments were performed using pyrrole and picoline reagents distilled in an inert atmosphere of nitrogen. The reagents were obtained from Matheson, Coleman & Bell.

The solvent-base systems were all prepared in a drybox under nitrogen atmosphere, using 100 ml. of distilled solvent (*t*-butyl alcohol or *N,N*-dimethylformamide) and essentially alcohol free potassium *t*-butoxide at various molarities of the base. Potassium *t*-butoxide was obtained from the Mine Safety Appliance Co. and analysis showed it to be above 98.5% pure. The major impurity was potassium carbonate. Half of the required volume of solvent was poured into a glass-stoppered graduated cylinder with the base slowly added under continuous agitation. As the limit of base solubility was approached the remaining portion of solvent was added and the base concentration was adjusted to the required molarity.

For experiments run under atmospheric pressure, weighed amounts of reactants were introduced into a specially adapted heavy-walled 500-ml. Erlenmeyer flask which had been previously flushed with nitrogen. The homogeneous solvent-base solution was then poured into the reactor flask.

(6) F. P. Richter, *et al.*, *Ind. Eng. Chem.*, **44**, 2601 (1952).