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## Free Radicals by Mass Spectrometry. XXV. Ionization Potentials of Cyanoalkyl Radicals

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The vertical ionization potentials of four cyano-substituted alkyl radicals have been measured by electron impact:  $\text{CNCH}_2$ , 10.87,  $\text{CNCHCH}_3$ , 9.76,  $\text{CNCH}_2\text{CH}_2$ , 9.85 and  $\text{CNC}(\text{CH}_3)_2$ , 9.15 v. The appearance potential of  $\text{CNCH}_2^+$  from  $\text{CH}_3\text{CN}$  gives  $\Delta H_f(\text{CNCH}_2^+) \leq 299$  kcal./mole, from which  $\Delta H_f(\text{CNCH}_2) \leq 48$  kcal./mole and  $D(\text{CNCH}_2\text{-H}) \leq 79$  kcal./mole. This low bond dissociation energy agrees with other evidence for the resonance stabilization of the  $\text{CNCH}_2$  radical and its homologs.

### Introduction

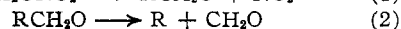
The effect of replacing H atoms in the methyl radical by  $\text{CH}_3$  groups is to reduce the ionization potential quite rapidly along the series: methyl, ethyl, isopropyl, *t*-butyl.<sup>2</sup> This effect can be quantitatively accounted for by a semi-empirical group-orbital calculation. For substitution by hetero-groups, however, there is as yet very little data available. The cyano-substituted alkyl radicals are such a series. This series of radicals is also of interest because of the possibility of stabilization by electron delocalization in some cases. An estimation of the C-H bond dissociation energy in  $\text{CH}_3\text{CN}$  would provide an indication of the magnitude of such an effect. Although there is chemical evidence for the weakness of C-H bonds in some nitriles, no estimates of the dissociation energies are available.

### Experimental

The cyanoalkyl radicals were generated by thermal decomposition of suitable derivatives in a fused silica capillary reactor leading directly into the ionization chamber of the mass spectrometer. This apparatus has been described previously.<sup>3</sup> The purified derivatives were held in a trap at 0° or some other convenient temperature and the vapor was admitted to the reactor through a stainless-steel adjustable valve. In this way the flow of vapor into the reactor could be held constant at a desired level for several hours. The customary pin-hole leak was not employed.

**Production of Radicals.**—In recent work it was found that the thermal decomposition of the nitrites  $\text{RCH}_2\text{ONO}$  was a convenient means for producing a radical R, where R was an alkyl<sup>2</sup> or cycloalkyl<sup>4</sup> radical. Attempts to prepare  $\text{CNCH}_2\text{CH}_2\text{ONO}$  from ethylene cyanohydrin and nitrous acid according to the usual method<sup>5</sup> were, however, unsuccessful. The nitrite decomposed immediately on formation. The nitrate was then prepared by the reaction of ethylene cyanohydrin with nitric acid in the presence of acetic anhydride.<sup>6</sup> Although this nitrate decomposed slowly on standing at room temperature, it could be stored without decomposition at 5°.

The decomposition of this, and other nitrates of the series, proceeded as<sup>7</sup>



In the present reactor, where the contact time is about  $10^{-8}$  sec., decomposition became appreciable at 350° and was

(1) National Research Council Postdoctorate Fellow, 1950-1960.

(2) F. P. Lossing and J. B. de Sousa, *J. Am. Chem. Soc.*, **81**, 281 (1959).

(3) J. B. Farmer and F. P. Lossing, *Can. J. Chem.*, **33**, 861 (1955).

(4) R. F. Pottie, A. G. Harrison and F. P. Lossing, *J. Am. Chem. Soc.*, **83**, 3204 (1961).

(5) "Organic Syntheses," Vol. XVI, John Wiley and Sons, Inc., New York, N. Y., 1936.

(6) G. Desseigne, *Bull. soc. chim. France*, 98 (1946).

(7) J. B. Levy, *J. Am. Chem. Soc.*, **76**, 3254, 3700 (1954).

complete at 700°. This range is the same as that observed for the alkyl nitrites.<sup>3</sup> The activation energies for decomposition of nitrites and nitrates appear to be roughly the same and are reported to be 35-39 kcal./mole.<sup>8</sup> No trace of the unstable intermediate  $\text{RCH}_2\text{O}$  could be found. An excellent yield of  $\text{CNCH}_2$  radical was obtained. Using 50 v. electrons, about 70% of the *m/e* 40 peak was attributable to the  $\text{CNCH}_2$  radical, the remainder arising from fragment ions of the dimer and acetonitrile formed by radical reactions. Using low electron energies, the ion current at *m/e* 40 increased by a factor of more than 100 as the furnace temperature was raised from 100 to 700°. No decrease from the maximum ion current occurred when the furnace was heated further to 900°.

The  $\text{CNCH}_2$  radical also was produced by thermal decomposition of succinonitrile and iodoacetonitrile. Although succinonitrile at 1000° was decomposed to the extent of only 20%, a sufficient yield of  $\text{CNCH}_2$  radical was obtained to allow a further measurement of the ionization potential. In this case the estimated error of measurement was somewhat greater. With iodoacetonitrile, prepared by refluxing chloroacetonitrile with KI in methyl alcohol solution,<sup>9</sup> the yield of radical was rather small. Presumably the back-reaction of  $\text{CNCH}_2$  with I atoms is quite fast. The yield was sufficient, however, to permit a measurement of  $I(\text{CNCH}_2)$  to be made in this case as well.

The  $\text{CNCHCH}_3$  radical was produced from the corresponding nitrate,  $\text{CNCH}(\text{CH}_3)\text{CH}_2\text{ONO}_2$ . This nitrate was prepared as follows. Dry HBr was reacted with methacrylonitrile, according to the method of Stevens,<sup>10</sup> to give  $\beta$ -bromoisobutyronitrile. The latter was dissolved in acetonitrile and  $\text{AgNO}_3$  was added.<sup>11</sup> After five days the precipitate was removed and the solution was distilled under vacuum. A small yield of  $\text{CNCH}(\text{CH}_3)\text{CH}_2\text{ONO}_2$  was obtained, which was further purified by fractionation at low pressures. This nitrate decomposed cleanly in the furnace to give a good yield of the  $\text{CNCHCH}_3$  radical, according to reactions 1 and 2 given above. As for  $\text{CNCH}_2$ , no decrease in the parent ion current for the radical was observed from 700-900°. Evidently this radical is rather stable with respect to loss of H to form acrylonitrile.

The  $\text{CNCH}_2\text{CH}_2$  radical was obtained from the thermal decomposition of  $\text{CNCH}_2\text{CH}_2\text{CH}_2\text{ONO}_2$ . This nitrate was prepared from  $\alpha$ -bromobutyronitrile by the action of  $\text{AgNO}_3$ . A good yield of radical was obtained by thermal decomposition of the nitrate. In contrast with the  $\text{CNCH}_2$  and  $\text{CNCHCH}_3$  radicals, however, a decrease in the parent ion current for the radical at low electron energies was observed above 550°. A corresponding large increase in the *m/e* 53 peak occurred above this temperature, evidently as a result of formation of acrylonitrile. Since no possibility exists for resonance stabilization in the  $\text{CNCH}_2\text{CH}_2$  radical, the stability with respect to H loss is much less than for the other radicals.

The  $\text{CNC}(\text{CH}_3)_2$  radical was prepared by the thermal decomposition of azo-*bis*-isobutyronitrile (AIBN). Some difficulty was encountered in the purification of this compound, and a clean spectrum at low furnace temperatures could not be obtained. Moreover, a small amount of dimer was formed, which could be a mixture of three

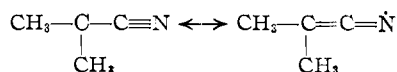
(8) P. Gray and A. Williams, *Chem. Revs.*, **59**, 239 (1959).

(9) S. Loy and S. F. Acree, *Am. Chem. J.*, **45**, 224 (1911).

(10) C. L. Stevens, *J. Am. Chem. Soc.*, **70**, 165 (1948).

(11) A. P. Ferris, K. W. McLean, I. G. Marks and W. D. Emmons, *ibid.*, **75**, 4078 (1953).

different compounds as a result of the hybrid structures for the radical



The formation of the "abnormal" dimer, dimethyl-N-(2-cyano-2-propyl) keteneimine, as an unstable intermediate in the reaction of cyanoisopropyl radicals has been demonstrated.<sup>12</sup> Since the spectra of these dimers is unknown, it was not possible to calculate the net parent peak intensity for the radical. Nevertheless, the cyanoisopropyl radical was formed in good yield, as shown by a large increase of the ion current of  $m/e$  68 at low electron energies with furnace temperatures above 350°. An approximate calculation of the net radical peak with 50 v. electrons, based on matching the slope of the lower part of ionization efficiency curves for  $m/e$  68 and for the xenon reference gas, showed that about 75% of the  $m/e$  68 peak could be attributed to the radical.

**Measurement of Ionization Potentials.**—The method used for measuring the ionization efficiency curves for the radical parent ion and the standard gas has been described previously.<sup>2</sup> For all except the  $\text{CNC}(\text{CH}_3)_2$  radical, the parent peak intensity for the radical with 50 v. electrons was calculated by subtracting the contributions of other products. The normalized ionization efficiency curves for radical and standard gas were then found to be parallel within  $\pm 0.05$  v. over the range from 0.1 to 5% of the 50 v. peak height. Since the net 50 v. peak height for the  $\text{CNC}(\text{CH}_3)_2$  radical could not be calculated for the reasons given above, the ionization efficiency curves of radical and standard were matched in curvature by vertical displacement. Since the normalized curves for the other radicals were found to be parallel, this procedure appears to be justified.

### Results and Discussion

The ionization potentials of the four cyanoalkyl radicals are given in Table I. The limits of error given are average deviations from the experimental mean, and do not represent limits of absolute error. In all cases the values are the mean of three or more determinations. The values for the ionization potential of  $\text{CNCH}_2$  radicals produced from the three different sources are in close agreement.

TABLE I  
IONIZATION POTENTIALS OF CYANOALKYL RADICALS

Radical	Radical source	Ionization potential (v.)
$\text{CNCH}_2$	$\text{CNCH}_2\text{CH}_2\text{ONO}_2$	$10.87 \pm 0.1$
	$\text{CNCH}_2\text{CH}_2\text{CN}$	$10.95 \pm .2$
	$\text{CNCH}_2\text{I}$	$10.86 \pm .2$
$\text{CNCHCH}_3$	$\text{CNCH}(\text{CH}_3)\text{CH}_2\text{ONO}_2$	$9.76 \pm .1$
$\text{CNCH}_2\text{CH}_2$	$\text{CNCH}_2\text{CH}_2\text{CH}_2\text{ONO}_2$	$9.85 \pm .1$
$\text{CNC}(\text{CH}_3)_2$	$\text{CNC}(\text{CH}_3)_2\text{N}=\text{NC}(\text{CH}_3)_2\text{CN}$	$9.15 \pm .1$

The effect of substitution of H and  $\text{CH}_3$  by CN on the ionization potentials of alkyl radicals<sup>2</sup> is shown in Table II. It can be seen that substitution of H by CN raises the ionization potential by about 1 v. and substitution of  $\text{CH}_3$  by CN raises it by about twice this amount. The decrease in ionization potential along the series cyanomethyl, cyanoethyl and cyanoisopropyl is intermediate between the decrease methyl > ethyl > isopropyl and ethyl > isopropyl > *t*-butyl. Although the fourth cyanoalkyl radical does not belong in this sequence, its ionization potential raises an interesting point. It seems clear from the evidence given above, *i.e.* that the  $\text{CNCH}_2\text{CH}_2$  radical decomposed above 700° while  $\text{CNCHCH}_3$  did not,

(12) M. Talât-Erben and S. Bywater, *J. Am. Chem. Soc.*, **77**, 3710 (1955); M. Talât-Erben and A. N. İsfendiyaroğlu, *Can. J. Chem.* **36**, 1158 (1958).

that there is no question as to the ionization potential being assigned to the wrong species as a result of isomerization of  $\text{CNCH}_2\text{CH}_2$  radical to  $\text{CNCHCH}_3$  radical. One must conclude, therefore, that the vertical ionization potentials of the two radicals are, in fact, nearly the same. The  $\text{CNCH}_2\text{CH}_2$  and  $\text{CNCHCH}_3$  radicals may be regarded as derivatives of ethyl radical formed by substituting CN for H on carbon atoms  $\beta$  and  $\alpha$ , respectively, to the carbon carrying the unpaired electron. On this basis some significant difference in ionization potential would be expected. Moreover, the  $\text{CNCHCH}_3$  radical is stabilized by electron delocalization while  $\text{CNCH}_2\text{CH}_2$  is not. Nevertheless these differences in structure, although unquestionably bringing about large differences in the heats of formation of the two radicals, are not reflected in the ionization potential.

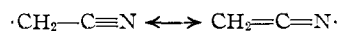
TABLE II  
EFFECT OF SUBSTITUTION ON IONIZATION POTENTIAL

Radical	H	Substituent X	
		$\text{CH}_3$	CN
$\dot{\text{C}}\text{H}_2\text{X}$	9.95	8.78	10.87
$\text{CH}_3\dot{\text{C}}\text{HX}$	8.78	7.90	9.76
$(\text{CH}_3)_2\dot{\text{C}}\text{X}$	7.90	7.42	9.15

**Heats of Formation of  $\text{CNCH}_2$  Radical and Ion.**—The appearance potential of  $\text{CNCH}_2^+$  ion from  $\text{CH}_3\text{CN}$  was found to be  $14.28 \pm 0.05$  v., in good agreement with an earlier measurement of 14.30 v.<sup>13</sup> Using  $A(\text{CNCH}_2^+) = 14.30 \pm 0.05$  v.,  $\Delta H_f(\text{CH}_3\text{CN}) = 21.0$  kcal./mole<sup>14</sup> and  $\Delta H_f(\text{H}) = 52.1$  kcal./mole<sup>14</sup> and the relation

$$A(\text{CNCH}_2^+) \geq \Delta H_f(\text{CNCH}_2^+) + \Delta H_f(\text{H}) - \Delta H_f(\text{CH}_3\text{CN})$$

one obtains  $\Delta H_f(\text{CNCH}_2^+) \leq 299$  kcal./mole. Then, from  $I(\text{CNCH}_2) = 10.87$  v.,  $\Delta H_f(\text{CNCH}_2) \leq 48$  kcal./mole and  $D(\text{CNCH}_2-\text{H}) \leq 79$  kcal./mole. This C-H dissociation energy is some 20 kcal./mole weaker than primary C-H bonds in alkanes and is nearly the same as for allylic C-H bonds.<sup>15</sup> This strongly suggests that the cyanomethyl radical possesses resonance stabilization of the same order as do allyl and benzyl radicals. The radical can therefore be written as a hybrid of two structures



Similarly, two resonating forms may be written for the  $\text{CNCHCH}_3$  and  $\text{CNC}(\text{CH}_3)_2$  radicals but not for  $\text{CNCH}_2\text{CH}_2$ . As noted above, the latter radical decomposed at temperatures above 550°, but the other three were stable to at least 900°.

Some chemical evidence for the stabilization of the cyanoalkyl radicals by electron delocalization has also been found. The bromination of nitriles with *N*-bromosuccinimide occurs smoothly for all members above  $\text{CH}_3\text{CN}$ , and even the latter can be brominated with this reagent under slightly more severe conditions.<sup>16</sup> *N*-bromosuccinimide is a rela-

(13) C. A. McDowell and J. W. Warren, *Trans. Faraday Soc.*, **48**, 1084 (1952).

(14) F. D. Rossini, *et al.*, "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," Carnegie Press, Pittsburgh, Pa., 1953.

(15) T. L. Cottrell, "The Strengths of Chemical Bonds," 2nd Ed., Butterworths Scientific Publications, London, 1958.

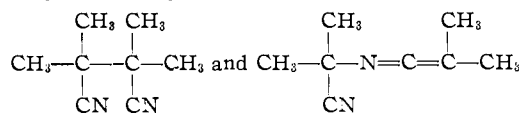
(16) P. Couvreur and A. Bruylants, *J. Org. Chem.*, **18**, 501 (1953).

tively mild brominating agent and is used to replace hydrogen atoms of the allylic type. The displacement takes place mainly on the carbon  $\alpha$  to the cyano group, as expected from resonance considerations.

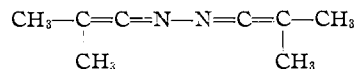
Experimental evidence has been obtained for the existence of a hybrid form for the cyanoisopropyl radical. In addition to the work of Talát-Erben and co-workers<sup>12</sup> mentioned above, Smith, *et al.*,<sup>17</sup> have recently identified two individual dimers of this radical as products in the thermal

(17) P. Smith and A. M. Rosenberg, *J. Am. Chem. Soc.*, **81**, 2037 (1959); P. Smith and S. Carbone, *ibid.*, **81**, 6174 (1959).

and photochemical decomposition of AIBN. The two dimers are tetramethyl succinonitrile and dimethyl-N-(2 cyano-2 propyl)-keteneimine



The third possible dimer, a diimine, was not ob-



served, presumably because of thermal instability.

[CONTRIBUTION FROM THE CONVAIR SCIENTIFIC RESEARCH LABORATORY, SAN DIEGO, CALIFORNIA, AND SAN DIEGO STATE COLLEGE, SAN DIEGO, CALIFORNIA]

## The Kinetics of the Manganate-Permanganate Exchange by N.m.r.

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The kinetics of the manganate-permanganate exchange reaction have been measured by the n.m.r. line broadening technique developed by McConnell and Weaver. The results indicate that in 1f potassium and sodium ion the reaction is first order with respect to each reactant. An activation energy of 8.3 kcal./mole was found in potassium ion system. These data are consistent with the results found from the tracer study of Sheppard and Wahl.

The kinetics of the manganate-permanganate exchange reaction have been studied extensively by tracer techniques<sup>1</sup> and found to be first order with respect to both manganate and permanganate ion concentrations. The rate was found to depend upon the nature (perhaps size) of the base cation present but was unaffected by the addition of other anions. Most of the work was done near 0° and at small reactant concentrations because of the speed of the reaction. Exchange half-times in the range 0.24–12.0 sec. were observed. McConnell and Weaver<sup>2</sup> developed the n.m.r. line broadening technique for the measurement of very rapid reactions and studied the rate of electron transfer between copper(I) and copper(II) ions in concentrated hydrochloric acid. A specific rate constant of  $5 \times 10^7 f^{-1} \text{sec.}^{-1}$  was observed. Giuliano and McConnell<sup>3</sup> studied the vanadium(IV)-vanadium(V) reaction in hydrochloric-perchloric acid mixtures by the same technique and found the specific rate constant for this reaction to be  $1.5 \times 10^6 f^{-2} \text{sec.}^{-1}$ . Both reactions are too rapid to be measured by even the most sophisticated tracer technique available at present.<sup>4</sup> It would be desirable to study a reaction where it would be possible to compare the n.m.r. method with the tracer technique. The manganate-permanganate exchange reaction appears to be the experimentally accessible reaction because it is rapid. In addition, manganese-55 possesses the desirable quality, for the purpose of measuring this reaction,

(1) J. C. Sheppard and A. C. Wahl, *J. Am. Chem. Soc.*, **79**, 1020 (1957).

(2) H. M. McConnell and H. E. Weaver, *J. Chem. Phys.*, **25**, 307 (1956).

(3) C. R. Giuliano and H. M. McConnell, *J. Inorg. and Nuclear Chem.*, **9**, 171 (1959).

(4) B. M. Gordon and A. C. Wahl, *J. Am. Chem. Soc.*, **80**, 273 (1958)

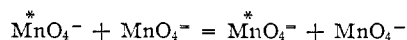
of high n.m.r. sensitivity as well as pure isotopic abundance.

The present investigation was undertaken to study the manganate-permanganate system using n.m.r. techniques for the purpose of comparison with and extension of the results of tracer studies as well as to verify the application of the n.m.r. method to chemical kinetic problems.

The observed width of the Mn-55 line of permanganate ion in sodium or potassium hydroxide solutions is about 20 millioersted (derivative peak-to-peak, corrected for modulation amplitude, modulation frequency, saturation and estimated field inhomogeneities in the Varian V-4012A 12-in. electromagnet<sup>5,6</sup>) and corresponds to a "natural" transverse relaxation time of  $T_2 \approx 8$  milliseconds according to the equation

$$1/T_2 = 0.866\gamma\Delta H \quad (1)$$

The paramagnetic manganate ion yields no observable nuclear resonance. The interaction between the nucleus and the unpaired electron of manganate ion shortens  $T_2$  to such an extent that the line width must be many thousands of oersteds. The "electron-transfer" process



will, therefore, introduce an additional mechanism to the "natural" transverse relaxation. Using the approximation that the life expectancy of a magnetic state after an exchange event is zero, McConnell's treatment<sup>2,7</sup> reduces to

$$\frac{1}{t_2} = \frac{1}{T_2} + \frac{1}{\tau} \quad (2)$$

(5) O. E. Myers and E. J. Putzer, *J. Applied Phys.*, **30**, 1987 (1959).

(6) O. E. Myers, *Bull. Am. Phys. Soc.*, **5**, 242 (1960).

(7) H. M. McConnell, *J. Chem. Phys.*, **28**, 430 (1958).