933. Pyrolyses of Ethyl Cyanide, t-Butyl Cyanide, Cumyl Cyanide, and Acetamide, and Bond Strengths in Cyanides

By Margaret Hunt, J. A. Kerr, and A. F. Trotman-Dickenson

Pyrolyses of the above cyanides and acetamide have been carried out by the aniline-carrier technique. Ethyl cyanide decomposes by three reactions yielding ultimately hydrogen, methane, and ethylene as gaseous products; the decomposition to give a methyl radical is a first-order homogeneous reaction with (686—765°): $\log k$ (sec.$^{-1}$) $= 14{\cdot}1 - (72{,}700/2{\cdot}3\boldsymbol{R}T)$. The analogous reaction for t-butyl cyanide has (602—652°): $\log k$ (sec.$^{-1}$) $= 15{\cdot}2 - (70{,}200/2{\cdot}3\boldsymbol{R}T)$. The rate-determining step for the production of methane in the pyrolysis of cumyl cyanide is of the first-order and homogeneous with (520—624°): $\log k$ (sec.$^{-1}$) $= 12{\cdot}3 - (54{,}100/2{\cdot}3\boldsymbol{R}T)$. The methane probably arises from bond rupture in the nitrile yielding a methyl radical, but it is possibly produced by direct molecular elimination. Acetamide decomposes mainly by the molecular elimination of ammonia for which the rate constant is (663—747°) $\log k$ (sec.$^{-1}$) $= 14{\cdot}7 - (73{,}400/2{\cdot}3\boldsymbol{R}T)$.

More reliable kinetic data on pyrolyses can be obtained if toluene is replaced by aniline in the toluene-carrier technique developed by Szwarc.[1] The problem of methane formation from the decomposition of toluene itself is completely eliminated and thus the method can be applied more readily to decompositions yielding methyl radicals. Previous Papers described the pyrolyses of alkylbenzenes,[2] *N*-methylanilines,[2,3] and phenylhydrazine;[3]

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[1] M. Szwarc, *J. Chem. Phys.*, 1949, **17**, 431.

[2] G. L. Esteban, J. A. Kerr, and A. F. Trotman-Dickenson, *J.*, 1963, 3873, 3879.

[3] J. A. Kerr, A. F. Trotman-Dickenson, and M. Wolter, *J.*, 1964, 3584.

here we report the pyrolyses of cyanides and acetamide. The cyanides were selected to investigate the effect of the CN group of the strength of C–C and C–H bonds and to obtain an independent value of the bond dissociation energy *D*(H–CH_2CN). Acetamide was pyrolysed to obtain information on the heat of formation of the acetyl radical.

EXPERIMENTAL

Apparatus and Procedure.—The experimental technique has been described.[2,3] Ethyl and t-butyl cyanide were injected into the carrier gas stream through a capillary stopcock; cumyl cyanide and acetamide were injected by evaporating aniline solutions of predetermined composition. Product mixtures of hydrogen and methane were analysed as before. When ethylene or ammonia was present in the products, gases non-condensable at liquid-air temperature were pumped off and then ethylene or ammonia was separated at −150° or −90°, respectively, and measured in the gas burette. Analyses for both gases were checked by gas chromatography. When carbon monoxide was present in the non-condensable fraction it was combusted to carbon dioxide, which was condensed at liquid-air temperature; the carbon monoxide was determined by difference.

Materials.—Commercial samples of ethyl and t-butyl cyanide, and acetamide were distilled twice and constant-boiling fractions collected. Cumyl cyanide was prepared by treating benzyl cyanide in benzene with finely divided sodium amide and methyl sulphate.[4,5] The product was twice distilled under vacuum and a constant-boiling fraction collected. Gas-chromatographic analysis revealed no impurities.

RESULTS AND DISCUSSION

The Pyrolysis of Ethyl Cyanide.—Results were obtained over a temperature range 686—765°, with contact times varying from 0·6 to 1·7 sec., and total pressures from 6 to 16 mm. As shown in Table 1 the gaseous products were methane, hydrogen, and ethylene. Since the weakest bond in ethyl cyanide is probably CH_3–CH_2CN, the mechanism for its

TABLE 1

The pyrolysis of ethyl cyanide

Temp. (°K)	Total pressure (mm.)	Contact time (sec.)	Cyanide	CH_4	H_2	C_2H_4	10^2k_1 (sec.$^{-1}$)
			10^{-5} mole				
958·8	15·8 *	1·70	192·6	0·950	1·94	0·767	0·282
961·4	11·9	1·33	427·4	1·90	3·65	1·80	0·326
972·2	15·6 *	1·68	199·9	1·81	3·16	1·24	0·544
973·3	15·7 *	1·72	215·9	1·81	3·78	1·25	0·497
976·5	11·9	1·33	402·7	3·15	6·23	2·75	0·589
978·0	7·1	0·69	119·3	0·669	0·895	0·355	9·795
982·5	15·5 *	1·62	197·9	3·41	5·07	1·45	0·764
992·8	9·3	0·64	375·6	2·62	3·39	2·40	1·11
993·3	9·5	0·65	397·6	2·81	3·54	2·69	1·09
996·5	15·6 *	1·62	188·1	4·05	7·65	1·89	1·38
998·0	9·9	0·62	356·6	3·42	4·18	2·68	1·58
1001·7	9·9	0·61	416·1	4·27	5·23	3·83	1·71
1005·7	10·0	0·62	387·8	4·01	5·44	3·70	1·69
1007·7	6·5	0·61	737·3	8·04	12·6	7·48	1·83
1008·3	15·6 *	1·67	206·8	6·19	10·1	2·97	1·88
1008·5	7·2	0·65	170·3	2·06	2·80	1·24	1·88
1008·8	10·3	0·61	305·4	4·14	5·84	3·70	2·27
1009·1	11·6	0·70	369·3	4·65	5·93	4·05	1·83
1019·8	10·1	0·62	340·4	6·23	7·98	5·83	3·08
1026·0	9·9	0·61	283·9	6·38	7·75	5·85	3·87
1037·7	9·9	0·59	372·7	10·0	12·8	9·60	4·77

* Packed vessel.

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[4] F. Bodroux and F. Taboury, *Bull. Soc. chim. France*, 1910, **7**, 670.

[5] G. Darzens and A. Levy, *Compt. rend.*, 1929, **189**, 1287.

pyrolysis in an excess of aniline, on the basis of previous results by this method, would be expected to be:

$$CH_3{\cdot}CH_2CN = CH_3{\cdot} + {\cdot}CH_2CN \tag{1}$$

$$CH_3{\cdot} + C_6H_5{\cdot}NH_2 = CH_4 + C_6H_5NH{\cdot} \tag{2}$$

$$2C_6H_5NH{\cdot} = (C_6H_5NH)_2 \tag{3}$$

This mechanism does not, however, account for the large amounts of hydrogen and ethylene also found in the products. They could arise from direct molecular-elimination reactions:

$$CH_3{\cdot}CH_2CN = H_2 + CH_2{=}CHCN \tag{4}$$

$$CH_3{\cdot}CH_2CN = C_2H_4 + HCN \tag{5}$$

First-order rate constants for the overall decomposition of the ethyl cyanide (k_{total}) were calculated from the yields of hydrogen, methane, and ethylene, in accordance with the above mechanism. Individual rate constants, k_1, k_4, and k_5 were then calculated from k_{total} and the fraction of the decomposition arising from each of the products. The rate constants k_1 were unaffected by changing the contact time, total pressure, and surface-to-volume ratio of the reaction vessel, and the Arrhenius plot of these rate constants yielded a good straight line. Clearly, reaction (1) is a first-order homogeneous decomposition. A least-mean-squares treatment gave

$$\log k_1 \text{ (sec.}^{-1}) = (14{\cdot}10 \pm 0{\cdot}30) - (72{,}700 \pm 1400/2{\cdot}3\boldsymbol{R}T)$$

The Arrhenius plots of the other two rate constants, k_4 and k_5, for the suggested molecular elimination processes, showed more scatter and the best straight lines correspond to:

$$\log k_4 \text{ (sec.}^{-1}) = 12{\cdot}4 - (64{,}600/2{\cdot}3\boldsymbol{R}T) \text{ and}$$
$$\log k_5 \text{ (sec.}^{-1}) = 15{\cdot}0 - (77{,}300/2{\cdot}3\boldsymbol{R}T).$$

These parameters are compatible with results on other molecular-elimination reactions.[6]

The Pyrolysis of t-Butyl Cyanide.—From Table 2 it is seen that this study was made between 602 and 652°, with contact times from 0·74 to 7·5 sec., and total pressures from 8·6 to 12 mm. Under these conditions the gaseous products were methane and hydrogen, but at higher temperatures ethane and ethylene were also produced. The high-temperature mechanism was not further investigated. Below 650° it seems likely that the mechanism to account for methane formation is:

TABLE 2

The pyrolysis of t-butyl cyanide

Temp. (°K)	Total pressure (mm.)	Contact time (sec.)	Cyanide	CH_4	H_2	10^2k_6 (sec.$^{-1}$)
			10^{-5} mole			
874·7	11·1	1·37	228·3	1·43	0·365	0·420
880·7	11·7	1·47	213·6	1·53	0·770	0·454
884·7	11·9	1·45	206·5	2·03	0·931	0·684
893·0	9·9	0·75	307·2	2·27	1·07	0·892
897·5	11·9	1·42	166·3	2·94	1·53	1·24
899·0	10·1	0·76	219·8	2·06	0·865	1·12
902·8 *	8·7	0·76	207·9	2·35	1·07	1·42
908·4	12·0	1·43	171·5	4·90	3·02	1·98
909·2 *	10·2	0·76	213·9	2·98	1·60	1·82
913·0	8·7	0·76	166·4	2·78	1·55	2·19
918·0	8·6	0·76	156·5	3·34	1·73	2·85
922·4	8·7	0·76	233·4	5·74	2·70	3·24
925·2	10·1	0·74	220·9	5·64	3·28	3·44

* Packed vessel.

$$(CH_3)_3CCN = (CH_3)_2\dot{C}CN + CH_3{\cdot} \tag{6}$$

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[6] A. F. Trotman-Dickenson, "Gas Kinetics," Butterworths' Scientific Publns., London, 1955, p. 129.

plus reactions (2) and (3). On this basis, first-order rate constants, k_6, were calculated from the yields of methane. Least-mean-squares treatment gave

$$\log k_6\ (\text{sec.}^{-1}) = (15{\cdot}16 \pm 0{\cdot}34) - (70{,}200 \pm 1400/2{\cdot}3\boldsymbol{R}T).$$

The values of k_6 were independent of contact time, total pressure of reactant, percentage decomposition of the cyanide, and surface-to-volume ration of the reaction vessel, showing that reaction (6) was first-order and homogeneous.

The relatively large amounts of hydrogen in the products may arise from the decomposition of the cyano-radical formed in reaction (6), *i.e.*,

$$\cdot C(CH_3)_2CN = \cdot CH_2\dot{C}(CH_3)CN + H\cdot \qquad (7)$$

$$H\cdot + C_6H_5\cdot NH_2 = H_2 + C_6H_5NH\cdot \qquad (8)$$

Approximate thermochemical calculations show that reaction (7) is feasible.

The Pyrolysis of Cumyl Cyanide.—This compound was pyrolysed between 520 and 624°.

TABLE 3

The pyrolysis of cumyl cyanide

Temp.	Total pressure	Contact time	Cumyl cyanide	CH_4	H_2	10^2k_9
(°K)	(mm.)	(sec.)	10^{-5} mole			(sec.$^{-1}$)
793·5	8·3 †	3·04	98·9	0·621	—	0·189
802·2	8·3 †	3·01	43·6	0·479	—	0·359
812·2	8·2 †	3·02	53·5	0·917	—	0·549
819·2	7·9 †	3·17	125·6	2·70	—	0·683
824·4	8·3 †	2·91	55·7	1·48	0·209	0·910
828·8	8·6 †	2·98	56·0	1·76	0·287	1·05
828·8	8·5*†	2·77	56·8	1·63	0·304	1·04
834·0	8·5 †	2·66	65·1	2·35	0·434	1·36
838·0	9·5	2·27	42·1	1·57	0·655	1·65
938·5	9·3	2·27	50·4	1·82	0·655	1·60
839·0	8·6 †	3·13	65·0	2·69	0·511	1·34
843·9	8·9 †	3·17	50·5	2·72	0·357	1·75
846·2	10·2	2·27	77·1	3·26	1·79	1·90
850·8	10·2	2·21	56·2	2·76	1·51	2·25
853·7	8·7*†	3·03	31·6	2·23	0·512	2·42
855·0	10·2	2·26	18·4	1·27	0·482	3·16
859·0	4·9 †	0·98	61·6	2·47	0·641	4·01
861·8	13·7	2·23	19·4	1·39	0·856	3·33
862·0	8·7 †	3·04	30·5	3·22	1·07	3·67
862·0	13·6	2·21	35·2	2·37	1·60	3·16
865·7	5·3 †	1·06	59·1	2·97	0·728	4·85
867·7	11·0	2·38	37·9	3·90	2·04	4·54
871·1	5·2	1·05	115·3	5·84	2·61	4·91
874·7	8·2	1·10	45·4	3·00	0·886	6·22
876·0	10·4	2·49	74·7	9·99	5·04	5·75
889·0	11·4	1·89	32·4	4·73	3·64	8·35
890·3	11·5	1·90	34·0	6·21	2·94	10·6
897·1	11·3	2·10	86·7	22·8	11·6	14·5

* Packed vessel. † 3,4-Dichlorotoluene as carrier gas.

Table 3 lists the other experimental conditions and analytical results, the products being methane and hydrogen. It was noticed that, after the aniline solutions of cumyl cyanide had been injected, a small solid deposit was left in the evaporating container. The deposit, which was negligible compared with the weight of cyanide, could not be analysed. To see if this deposit had any effect upon the kinetic results, runs were carried out with 3,4-dichlorotoluene, which left no deposit, as carrier gas. As shown in Table 3 the rate constants were independent of the carrier gas. Previous results indicate the reaction

$$C_6H_5\cdot C(CH_3)_2CN = C_6H_5\cdot\dot{C}(CH_3)CN + CH_3\cdot \qquad (9)$$

followed by reactions (2) and (3), to account for the methane formation. The mechanism of formation of the hydrogen is again unknown. First-order rate constants k_9 were calculated from the yields of methane, and shown to be independent of contact time, overall pressure, and packed reaction vessel. Least-mean-squares calculation of the results gave

$$\log k_9\ (\text{sec.}^{-1}) = (12{\cdot}30 \pm 0{\cdot}06) - (54{,}100 \pm 700/2{\cdot}3\boldsymbol{R}T)$$

The *A*-factor thus obtained is much lower than that found for analogous reactions of the other cyanides. This may indicate that in the pyrolysis of cumyl cyanide methane is formed by a direct molecular elimination, since a four-centre activated complex could be involved. No definite choice of mechanism is possible from our experiments.

The Pyrolysis of Acetamide.—Table 4 lists the analytical results and experimental conditions. The main gaseous product was ammonia, with small amounts of hydrogen, methane, and carbon monoxide. Obviously the kinetically interesting decomposition, yielding acetyl and amino-radicals, is a minor process. The approximate equality of the methane and carbon monoxide products does suggest, however, that they arise from this decomposition and subsequent reactions:

TABLE 4

The pyrolysis of acetamide

Temp. (°K)	Total pressure (mm.)	Contact time (sec.)	Acetamide	NH_3	CO	CH_4	10^2k_{12} (sec.$^{-1}$)
			10^{-5} mole				
936·2 *	9·5	2·18	104·9	0·854	0·070	0·081	0·332
938·5	11·6	2·00	86·2	0·583	0·072	0·064	0·342
943·3 *	9·7	2·02	51·1	0·612	0·082	0·040	0·582
945·7 *	10·3	2·23	50·9	0·555	0·051	0·044	0·454
949·0	11·6	1·99	255·3	3·38	0·199	0·221	0·741
959·8	11·6	1·20	87·5	1·25	0·189	0·145	0·694
970·0	11·2	1·91	159·6	3·49	0·335	0·213	1·14
977·3	12·0	2·00	100·1	2·63	0·200	0·198	1·32
980·0	12·4	2·13	57·9	1·95	0·280	0·322	1·71
995·5	12·3	1·87	69·6	2·72	0·080	0·094	2·12
1001·0	10·9	2·07	202·8	21·1	—	—	5·29
1007·5	12·0	2·03	85·5	10·9	0·332	0·289	6·75
1019·7	11·7	2·07	76·4	13·4	0·500	0·634	16·6

* Packed vessel.

$$CH_3{\cdot}CONH_2 = CH_3{\cdot}CO{\cdot} + NH_2{\cdot} \qquad (10)$$

$$CH_3{\cdot}CO{\cdot} = CH_3{\cdot} + CO \qquad (11)$$

$$CH_3{\cdot} + C_6H_5{\cdot}NH_2 = CH_4 + C_6H_5NH{\cdot} \qquad (2)$$

Unfortunately, owing to the small amounts of methane and carbon monoxide in the products, it was not possible to treat reaction (10) quantitatively.

The large amounts of ammonia appear to arise from a direct molecular elimination:

$$CH_3{\cdot}CONH_2 = CH_2CO + NH_3 \qquad (12)$$

No attempt was made to detect the keten; it may have polymerised outside the reaction zone. First-order rate constants (k_{12}), calculated from the total yields of ammonia, were found to be independent of the usual variables. The following equation was obtained from the Arrhenius plot, which gave a good straight line:

$$\log k_{12}\ (\text{sec.}^{-1}) = 14{\cdot}7 - (73{,}400/2{\cdot}3\boldsymbol{R}T)$$

The *A*-factor and activation energy are reasonably in line with other published data on molecular elimination reactions.[6]

Bond Strengths in Cyanides.—The bond dissociation energy $D(CH_3\text{–}CH_2CN)$ can be taken as equal to the preceding activation energy for the decomposition of ethyl cyanide [reaction (1)], by making the assumption that the activation energy for the reverse radical combination reaction is zero. Hence from the equation:

$$D(CH_3\text{–}CH_2CN) = \Delta H_f^\circ(CH_3) + \Delta H_f^\circ(CH_2CN) - \Delta H_f^\circ(C_2H_5CN)$$

the heat of formation of the cyanomethyl radical can be calculated. Taking $\Delta H_f^\circ(\text{Me}) = 33{\cdot}9$ and $\Delta H_f^\circ(C_2H_5CN) = 11{\cdot}5$ kcal. mole^{-1}, we get $\Delta H_f^\circ(CH_2CN) = 50{\cdot}3$ kcal. mole^{-1}. This value, in turn, yields $D(CN{\cdot}CH_2{-}H) = 81{\cdot}4$ kcal. mole^{-1} from [7] ΔH_f° $(CH_3{\cdot}CN) = 21{\cdot}0$ kcal. mole^{-1}.

From our results $D(CN{\cdot}CH_2{-}H) - D(CN{\cdot}CH_2{-}CH_3) = 81{\cdot}4 - 72{\cdot}7 = 8{\cdot}7$ kcal. mole^{-1}. Analogous differences between C–H and C–CH_3 bond strengths are readily calculated for other compounds from the heats of formation of the hydrogen atom (52·1 kcal. mole^{-1}) and methyl radical (33·9 kcal. mole^{-1}) and the heats of formation of the parent compounds (RH and RCH_3). Thus

$$\begin{aligned} D(R{-}H) - D(R{-}CH_3) &= [\Delta H_f^\circ(H) - \Delta H_f^\circ(CH_3)] - [\Delta H_f^\circ(RH) - \Delta H_f^\circ(RCH_3)] \\ &= 18{\cdot}2 - [\Delta H_f^\circ(RH) - \Delta H_f^\circ(RCH_3)] \end{aligned}$$

The results of such calculations are given in Table 5.

TABLE 5

[$D(R{-}H) - D(R{-}CH_3)$] values (in kcal. mole^{-1}) for a series of compounds, RH and RCH_3

Radical R	ΔH_f° (RH)	ΔH_f° (RCH_3)	$D(R{-}H) - D(R{-}CH_3)$	Radical R	ΔH_f° (RH)	ΔH_f° (RCH_3)	$D(R{-}H) - D(R{-}CH_3)$
$C_2H_5{\cdot}$	−20·2	−24·8	13·6	$CN{\cdot}$	31·2	21·0	8·0
$CH{=}CH{\cdot}CH_2{\cdot}$	4·9	0·3	13·6	$CH_2{=}CH{\cdot}$	12·5	4·9	10·6
$CH{\equiv}C{\cdot}CH_2{\cdot}$ ...	44·3	39·7	13·6	$CH{\equiv}C{\cdot}$	54·2	44·3	8·3
$C_3H_7{\cdot}$	−24·8	−29·8	13·2	$HCO{\cdot}$	−27·7	−39·8	6·1
$C_6H_5CH_2{\cdot}$	12·0	7·1	13·3	$CH_3CO{\cdot}$.........	−39·8	−51·8	6·2
$CH_2Cl{\cdot}$	−19·6	−25·1	12·7	$C_6H_5{\cdot}$............	19·8	12·0	10·4
$HCOCH_2{\cdot}$	−39·8	−46·0	12·0				
$CH_3{\cdot}COCH_2{\cdot}$ ...	−51·8	−58·2	11·8				

As shown by the first column of differences, [$D(C{-}H) - D(C{-}CH_3)$] appears to be fairly constant at about 13 kcal. mole^{-1} provided the H atom and CH_3 group are attached to a CH_2 group. Lower differences are found only when the bonds are formed between H or CH_3 and other groups. On this basis, the value deduced here for $D(CN{\cdot}CH_2{-}H) - D(CN{\cdot}CH_2{-}CH_3)$ is a considerable underestimate.

If it is assumed that the activation energy for the pyrolysis of ethyl cyanide is correct, any error involved must arise from the thermochemical data used to deduce $D(CN{\cdot}CH_2{-}H)$. There is no reason for doubting the heat of formation of methyl cyanide quoted by Roberts and Skinner,[7] since the determination is fairly recent. The heat of formation of ethyl cyanide, as calculated by Szwarc and Taylor,[8] on the other hand, may be wrong since it ultimately depends on the heat of combustion of ethyl cyanide determined by Lemoult [9] in 1909. Early combustions of nitrogen-containing compounds are notoriously unreliable. Lemoult's value for the heat of combustion of hydrazobenzene,[10] for instance, was found to be approximately 1·5% too high.[11] A combustion of ethyl cyanide by modern techniques would resolve this difficulty, but until then a value of $D(CN{\cdot}CH_2{-}H) = 72{\cdot}7 + 13 = 85{\cdot}7$ kcal. mole^{-1} is the best available.

It is difficult to see why, however, the recent determination by Pottie and Lossing [12] of $D(CN{\cdot}CH_2{-}H) \leqslant 79$ kcal. mole^{-1} from electron-impact studies on $CN{\cdot}CH_2$-substituted compound, should be in error.

If it is assumed that the value $D(CN{\cdot}CH_2{-}H)$ reported here is a minimum value, the difference in C–H bond strengths in methane [13] and ethyl cyanide, $\geqslant 22{\cdot}6$ kcal. mole^{-1}, can be taken as a measure of the resonance energy of the cyanomethyl radical. Other

[7] J. S. Roberts and H. A. Skinner, *Trans. Faraday Soc.*, 1949, **45**, 339.

[8] M. Szwarc and J. W. Taylor, *Trans. Faraday Soc.*, 1951, **47**, 1293.

[9] P. Lemoult, *Compt. rend.*, 1909, **148**, 1602.

[10] P. Lemoult, *Ann. Chim. Phys.*, 1908, **14**, 184.

[11] L. G. Cole and E. C. Gilbert, *J. Amer. Chem. Soc.*, 1951, **73**, 5423.

[12] R. F. Pottie and F. P. Lossing, *J. Amer. Chem. Soc.*, 1961, **83**, 4737.

[13] G. C. Fettis and A. F. Trotman-Dickenson, *J.*, 1961, 3037.

corresponding values are benzyl[2] = 18·9, anilino[2] = 23·0, and allyl[14] = 20·0 kcal. mole^{-1}.

From the pyrolysis of t-butyl cyanide the strength of the bond $D[CH_3-C(CH_3)_2CN]$ is 70·2 kcal. mole^{-1}, but no further deductions can be made concerning the heat of formation of the $\cdot C(CH_3)_2CN$ radical until the necessary thermochemical data become available.

Provided the mechanism for the pyrolysis of cumyl cyanide involves a $C-CH_3$ bond rupture, then the dissociation energy $D[CH_3-C(CH_3)(CN)C_6H_5]$ = 54·1 kcal. mole^{-1}.

The effect of CN substitution on C–C bonds can now be seen from Table 6.

TABLE 6

Effect of CN substitution on C–C bond dissociation energies (kcal. mole^{-1})

Bond	Dissociation energy (*D*)	Differences in *D*	Bond	Dissociation energy (*D*)	Differences in *D*
CH_3-CH_3	88·0 *	5	CH_3-CH_2CN	73	2·8
$CH_3-CH(CH_3)_2$	83·0 *	17	$CH_3-C(CH_3)_2CN$	70·2	19
$CH_3-CH(CH_3)C_6H_5$ ...	66·0 †		$CH_3-C(CN)(CH_3)C_6H_5$	54·1	

* Calculated from ΔH_f° (Me) = 33·9 and ΔH_f° (Pr^i) = 17·6 kcal. mole^{-1} (ref. 13). † Ref. 3.

Obviously the introduction of a CN group into a molecule considerably weakens the adjacent C–C bond and the effect is fairly consistent throughout the short series of compounds studied.

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EDWARD DAVIES CHEMICAL LABORATORY,
ABERYSTWYTH, WALES.

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[14] S. W. Benson, A. N. Bose, and P. Nangia, *J. Amer. Chem. Soc.*, 1963, **85**, 1388.