

its free volume, and $V_0 = V - V_f$ the "occupied" volume, we could assign to V_0 a temperature coefficient which must be in some way related to $^{3/2} (d \ln \bar{r}_0^2)/dT$.

However, it must be stressed that this tentative interpretation is unfortunately connected with factors which are at present almost totally unknown; for instance, one of these factors is chain mobility below T_g .

In particular, what is of more concern here is not the intermolecular mobility (*i.e.*, movements of one molecule in respect to another, which we know to be almost absent at temperatures below T_g), but intramolecular mobility, that is, the ability of chain segments to change

their conformations when temperature changes, below T_g .

This problem, which we consider of the foremost importance for the study of glass properties, is now receiving attention in our institute.

Acknowledgment. The author thanks Prof. C. Rossi for his constant encouragement and advice given during this work, and also thanks his colleagues of this institute for helpful discussions. The author also wishes to express his gratitude to Mr. A. Turturro and Mr. L. Planitario, who have skillfully attended to the experimental work almost day and night for more than 3 months.

The Reactions of CN Radicals in the Gas Phase

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Competitive rate constants have been obtained for the reaction of CN radicals with methane, ethane, and propane by the photolysis of ICN in the presence of mixtures of these hydrocarbons. It has not proved possible to establish absolute rate constants for any of these reactions, but it would seem that CN radicals abstract hydrogen from hydrocarbons about as easily as do chlorine atoms. Other sources of CN radicals and the addition of CN radicals to olefins have been studied qualitatively. An improved preparation of solvent-free ICN is reported.

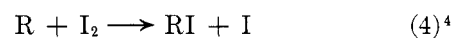
Preliminary Qualitative Experiments

Photolytic dissociation of ICN vapor at 2537 Å. leads to an iodine atom and a CN radical. The useful temperature range is somewhat limited, roughly 30–150°, since above 150° the equilibrium



is too far over to the right,¹ and, below 30°, the vapor pressure is too low.² BrCN is much more volatile and is photolyzed in the same way, but nothing is gained because its extinction coefficient is lower³ than that of ICN by a factor of 100. If a mixture of a hydrocarbon RH and ICN vapor is photolyzed in

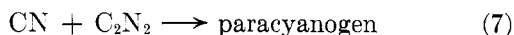
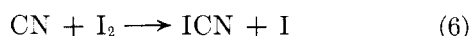
a quartz vessel with a low pressure mercury lamp, the products, apart from I_2 and C_2N_2 formed in reaction 1, are RI, HCN, a little RCN, and some paracyanogen. These can be explained by a scheme of reactions including



(1) G. N. Lewis and D. B. Keyes, *J. Am. Chem. Soc.*, **40**, 472 (1918).

(2) D. R. Stull, *Ind. Eng. Chem.*, **39**, 517 (1947).

(3) A. E. Gillam, *Trans. Faraday Soc.*, **29**, 1132 (1933).



The addition of excess iodine to the original reaction mixture favors reactions 4 and 6 over reactions 5 and 7 and suppresses completely the formation of RCN. This means that the rate of formation of RI is equal to the rate of formation of R radicals and leads to considerable simplifications analytically. It must be remembered however that the photolysis of I_2 and RH alone under these conditions leads to considerable yields of RI *via* excited iodine molecules⁵ unless all the 1849-Å. radiation is filtered out—this is easily done using a 5-cm. path length of deionized water. It is also important to notice that the establishment of the equilibrium 1 does not involve radicals, since the above products are not formed if RH and ICN are heated together at temperatures up to 150°.

A few exploratory experiments were carried out in which ICN was photolyzed in the presence of ethylene and propylene. With ethylene, the products were mainly HCN and acrylonitrile; also formed were some ethyl iodide and an unidentified substance which contained iodine and eluted from the chromatograph between HCN and EtI; the latter product was absent if H_2 was used as the chromatographic carrier gas and was probably vinyl iodide. Using propylene, α -methylacrylonitrile and allyl iodide were among the products; α -methylvinyl iodide was probably also formed since *i*-PrI appeared if H_2 was used as the carrier gas in the analysis. These products do not occur in the absence of photolysis and can readily be accounted for by radical mechanisms.

Relative Rate Constants

About 0.2 g. of ICN, 0.4 g. of I_2 , and 5–10 cm. of the hydrocarbon mixture under investigation were photolyzed at 2537 Å. in a 250-ml. quartz flask for periods of 3–10 hr. The hydrocarbon mixtures studied were methane-ethane and ethane-propane, and the proportions were chosen to yield approximately equal amounts of the corresponding iodides; propane was also used alone, and the products were analyzed for *n*-PrI and *i*-PrI. The analyses were carried out using a gas chromatograph with thermistor detectors and hydrogen as a carrier; almost any column packing will do. It is, of course, necessary to consider what correction must be made for the fact that alkyl iodides are readily decomposed by ultraviolet radiation, and blank experiments were carried out to determine the correction. It was found that MeI was unaffected by irradiation at 2537 Å. in the presence of the large

excess of I_2 and ICN which was always present (*cf.* footnote 4). EtI was unaffected below 100°, but the two propyl iodides were decomposed at measurable rates at all temperatures. In all three of these cases, the rate of decomposition was markedly temperature dependent, and the appropriate corrections were made after suitable calibration at each temperature, on the assumption that the rate of formation of the iodides was constant with time; provided sufficient time was allowed for reaction 1 to reach equilibrium, this should have been so. The relative rate constants obtained for methane-ethane mixtures are shown in Figure 1, but in the other experiments it was impossible

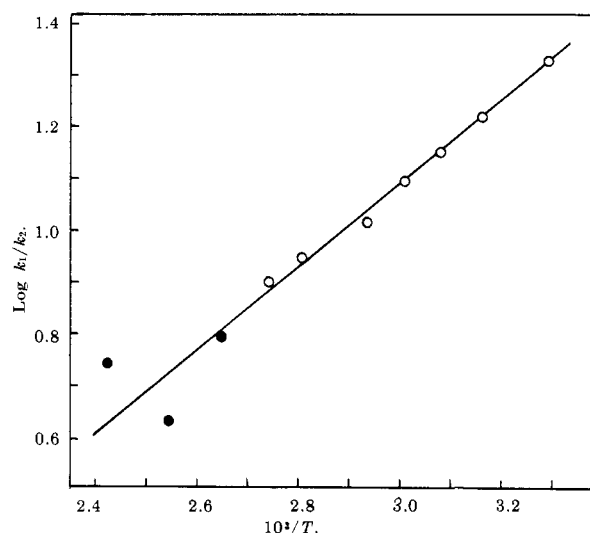


Figure 1. Arrhenius plot of relative rate constants for attack of CN radicals on ethane (1) and methane (2). The three closed-in circles represent experiments in which a correction was made for loss of EtI during the photolysis.

to distinguish any meaningful temperature coefficient. The corresponding Arrhenius parameters are summarized in Table I. The activation energy differences may be compared with those for halogen atom abstraction reactions which are collected together in Table II, and they appear to be most nearly like those for chlorine. Consequently, they are not inconsistent with the value of $E = 7$ kcal. for $CN + H_2 \rightarrow HCN + H$ suggested by Hartel and Polanyi⁶ from their sodium flame studies. Unfortunately, we were unable to

(4) $R + ICN \rightarrow RI + CN$ is thermochemically very unfavorable, and separate experiments using di-*t*-butyl peroxide as a thermal source of methyl radicals show that $R + ICN \rightarrow RCN + I$ does not go very easily.

(5) T. A. Gover and J. E. Willard, *J. Am. Chem. Soc.*, **82**, 3816 (1960).

(6) H. v. Hartel and M. Polanyi, *Z. physik. Chem.*, **B11**, 97 (1930).

make satisfactory measurements on H_2-CH_4 mixtures for reasons outlined below.

Table I: Relative Arrhenius Parameters for CN Abstraction Rates

Mixture	A_1/A_2^a	$E_1 - E_2$, kcal.
Me-H(1)-Et-H(2)	20.6	3.7 ± 0.2
Et-H(1)- <i>n</i> -Pr-H(2)	1.0	-0.1 ± 0.2
Et-H(1)- <i>i</i> -Pr-H(2)	1.1	-0.1 ± 0.3
<i>n</i> -Pr-H(1)- <i>i</i> -Pr-H(2)	1.2	-0.1 ± 0.3

^a Per molecule, *not* per hydrogen atom.

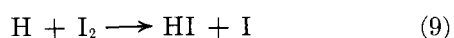
Table II: Activation Energies for Halogen Abstraction Reactions (kcal./mole)

R-H	Br ^a	Cl ^b	F ^c
H ₂	18.0	5.5	1.7
Me-H	18.3	3.9	1.2
Et-H	13.4	1.0	0.3
<i>n</i> -Pr-H	...	1.0	0
<i>i</i> -Pr-H	10.1	0.7	0

^a G. C. Fettis, J. H. Knox, and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 4177 (1960). ^b J. B. Pyke, H. O. Pritchard, and A. F. Trotman-Dickenson, *J. Am. Chem. Soc.*, **77**, 2629 (1955); J. H. Knox and R. L. Nelson, *Trans. Faraday Soc.*, **55**, 937 (1959). ^c P. D. Mercer and H. O. Pritchard, *J. Phys. Chem.*, **63**, 1468 (1959); G. C. Fettis, J. H. Knox, and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 1064 (1960).

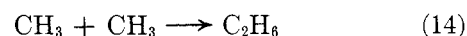
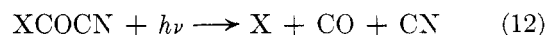
Absolute Rate Constants⁷

In their original search for a source of CN radicals, Galvin and Pritchard⁸ rejected the use of ICN because the existence of the equilibrium with I₂ and C₂N₂ eliminated the possibility of estimating the CN radical concentration from the rate of formation of C₂N₂. However, it has become increasingly clear during the course of our studies that, if the CN radical concentration is high enough to produce measurable amounts of C₂N₂, polymerization *via* reaction 7 inevitably follows. In the absence, therefore, of any simple route to absolute rate constants, it would seem that a further study of the C₂N₂-H₂ reaction⁹ might, at least in principle, yield values to which our results could be related through a study of H₂-CH₄ mixtures. In the presence of H₂, we have



Reaction 11 is virtually instantaneous, and the equilibrium is well over to the right (*cf.* ref. 1 for information about this reaction in solution). Hence, the rate of reaction of CN with H₂ is simply given by $1/2(R_{HCN} - R_{MeI})$. Unfortunately, this expression is not zero when H₂ is absent because small amounts of HCN appear to be produced by a thermal reaction of C₂N₂ with the walls of the vessel. Repeated ageing of the quartz vessel with C₂N₂ did not appear to reduce the rate of formation of HCN, nor did coating with concentrated H₂SO₄ or H₃PO₄. Metal vessels are equally unsatisfactory, and the deposition of a thin Teflon coating did not improve the situation significantly. Experiments in which small amounts of water vapor were added to reaction mixtures showed that CN radicals themselves react less readily with H₂O than with CH₄.

An alternative approach to the problem might be to use a system containing little or no cyanogen, *e.g.*, to photolyze some substance XCOCN (where X does not contain H atoms); thus



The rate of reaction 16 cannot be measured, but, assuming there are no third-body restrictions, it may be estimated using the relation $R_{C_2N_2}^{1/2} = R_{CH_3CN}/2R_{C_2H_6}^{1/2}$, through which $k_{13}/k_{16}^{1/2}$ may be obtained. Trichloroacetyl cyanide¹⁰ was tried, but as with other perchloro compounds,¹¹ chlorine atoms were a major product of the photolysis. Trifluoroacetyl cyanide dimer¹² [CF₃COCN]₂, on the other hand, did appear to yield CF₃ and CN radicals cleanly, but, even in the

(7) "Absolute" is used here to mean rate constants relative to the rate of recombination, $CN + CN \rightarrow C_2N_2$, which is assumed, in the absence of experimental evidence to the contrary, to take place every collision without any third-body restriction.

(8) J. P. Galvin and H. O. Pritchard, *J. Phys. Chem.*, **68**, 1035 (1964); J. P. Galvin, Ph.D. Thesis, Manchester, 1963.

(9) N. C. Robertson and R. N. Pease, *J. Am. Chem. Soc.*, **64**, 1880 (1942).

(10) P. Hofferichter, *J. prakt. Chem.*, **20**, 196 (1879).

(11) D. M. Tomkinson, J. P. Galvin, and H. O. Pritchard, *J. Phys. Chem.*, **68**, 541 (1964).

(12) R. H. Patton and J. H. Simons, *J. Am. Chem. Soc.*, **77**, 2016 (1955).

absence of any hydrogen-containing reactant, spurious HCN was formed. Similar difficulty was encountered by McElcheran, Wijnen, and Steacie¹³ in the photolysis of $\text{CO}(\text{CN})_2$, and it would appear to be quite a general problem which must be overcome before further progress can be made towards absolute rate parameters. Although CF_3 is relatively unreactive compared to CN, we did not think the indirect estimation of the extent of reaction 13 as $(2R_{\text{C}_2\text{H}_6} + R_{\text{CH}_3\text{CN}} + R_{\text{CF}_3\text{CH}_3})$, together with the indirect estimation of reaction 16 already proposed, was worthwhile at this stage.

Preparation of ICN

Solid I_2 plus excess solid $\text{Hg}(\text{CN})_2$ are sealed in an evacuated Pyrex tube. The tube is submerged in hot water until the color of iodine disappears (about 0.5–1.5 hr.⁵). Half the tube is then raised out of the water, when pure ICN needles deposit on the cool parts. This preparation is much faster and much more convenient than the conventional methods using solvents. The method also works for BrCN.

(13) D. E. McElcheran, M. H. J. Wijnen, and E. W. R. Steacie, *Can. J. Chem.*, **36**, 321 (1958).

Contact Angle Hysteresis. IV. Contact Angle Measurements on Heterogeneous Surfaces¹

by Robert H. Dettre and Rulon E. Johnson, Jr.

Contribution No. 316 from the Experimental Station, Organic Chemicals Department, E. I. du Pont de Nemours and Company, Wilmington 98, Delaware (Received September 5, 1964)

The wettability of a heterogeneous surface was studied as a function of coverage by regions of different intrinsic wettabilities. The observed behavior shows good agreement with that of an idealized heterogeneous surface.

Introduction

In a previous paper² we reported the results of a computer study of the effect of surface heterogeneity on the wettability of an idealized heterogeneous surface. The surface was one having regions of different intrinsic wettabilities, each region being larger than molecular dimensions. The analysis of this model surface showed that many metastable liquid-drop configurations are possible, each having a different contact angle and each separated from the next by an energy barrier. These energy barriers hinder the attainment of a configuration of minimum free energy. It was suggested that an observed configuration would depend on whether the drop periphery is advancing over the solid surface or receding from it and also on any vibration which

could cause the periphery to move. It was also suggested that, for a heterogeneous surface of two components, the observed contact angle will usually be different from the angle, ϕ , given by Cassie's³ equation

$$\cos \phi = \sigma_1 \cos \theta_1 + \sigma_2 \cos \theta_2 \quad (1)$$

where ϕ is the contact angle for the configuration of minimum free energy, σ_1 is the fraction of the surface having intrinsic contact angle θ_1 , and σ_2 is the fraction having intrinsic angle θ_2 . The advancing angle will

(1) Presented in part at the Gordon Research Conference on Chemistry at Interfaces, July 1961.

(2) R. E. Johnson, Jr., and R. H. Dettre, *J. Phys. Chem.*, **68**, 1744 (1964).

(3) A. B. D. Cassie, *Discussions Faraday Soc.*, **3**, 11 (1948).