of the stability of the Cr(II)–SCN$^-$ complex indicates that under the conditions of our experiments about 20% of the Cr(II) present existed in complexed form. Since the EDTA reaction appears to be much more than five times faster than the SCN$^-$ reaction, it seems that the differences in rates cannot be primarily due to differences in concentrations of the reducing agent. The effect of the ligand on the electronic energy levels of the metal atoms in the bridged complex is an important effect which is difficult to evaluate precisely.[17]

The free energy change for the catalytic reaction in question is directly related to the stability constant of the Cr(III) complex formed by the reaction. Unfortunately, there is little data on stability constants of either Cr(III) or Cr(II) complexes,[18] owing to the slow approach to equilibrium characteristic to the former and to the sensitivity of the latter to air oxidation. The ability of EDTA to form extremely stable complexes is well known; there is evidence[19] that pyrophosphate ion forms more stable complexes with $+3$ ions than does phosphate. Citrate appears to form more stable complexes than does tartrate.[18] The thiocyanato complex of Cr^{+3} has been shown to have a stability constant[11] which is less than that measured for the corresponding fluoro complex.[20] The sulfato complex is much less stable than the phosphato complex.[21]

The observed order of increasing rate of catalytic reactions is the same as the apparent order of stabilities of the Cr(III) complexes involved. This indicates that the rates of reactions of this type may be related to the free energy change for the reaction as was found to be the case in the more complex oxidations studied by Irvine.[6]

Acknowledgements.—The authors are indebted to Professor Henry Taube for helpful discussion. Support of the Smith, Kline and French Foundation through a research grant is also gratefully acknowledged.

[17] (a) R. A. Marcus, *Can. J. Chem.*, **37**, 155 (1959).

[18] J. Bjerrum, *et al.*, Eds., "Stability Constants," The Chemical Society (London), 1957.

[19] S. Mayer and S. D. Schwartz, THIS JOURNAL, **72**, 5106 (1950).

[20] A. S. Wilson and H. Taube, *ibid.*, **74**, 3509 (1952).

[21] A. Holroyd and J. E. Salmon, *J. Chem. Soc.*, 269 (1956).

[CONTRIBUTION FROM THE KINETICS AND COMBUSTION DIVISION OF ATLANTIC RESEARCH CORPORATION, ALEXANDRIA VIRGINIA]

The Thermal Decomposition of 2,2′-Azoisobutane[1]

BY JOSEPH B. LEVY AND B. K. W. COPELAND

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The thermal decomposition of gaseous 2,2′-azoisobutane has been studied over the temperature range 180–220°. The principal reaction products were isobutane and nitrogen. Small amounts of methane and 2,2,3,3-tetramethylbutane were also found. A brown solid deposit was invariably formed on the walls. Good first-order kinetics were observed and the temperature dependence of the rate measured. The activation energy of the reaction was found to be 42.8 kcal./mole and the frequency factor 2.2×10^{16} sec.$^{-1}$. In the presence of added nitric oxide, a blue product believed to be 2-methyl-2-nitrosopropane was formed and isobutene and nitrous oxide were observed as products. Experiments with added isobutene showed that it was consumed in the reaction. The significance of these results is discussed and a mechanism for the reaction proposed.

Introduction

The synthesis of 2,2′-azoisobutane and its thermal decomposition in dioctyl phthalate solution containing dihydroanthracene as a hydrogen donor have been described by Farenhorst and Kooyman.[2] It seemed that this compound should be a good source of *t*-butyl radicals since the decomposition temperature indicated was low, 200°, and nitrogen should be the only product other than *t*-butyl radicals. The thermal decomposition of 2,2′-azoisobutane in the gas phase was, therefore, investigated and the results are reported here.

Experimental

Chemicals.—The synthesis of 2,2′-azoisobutane was carried out as described by Farenhorst and Kooyman.[2] The product was fractionated through a short Vigreux column and the product boiling at 108–109° was that used in the experiments. The density was d^{20}_{4} 0.7617 compared to d^{20}_{4} 0.7670.[2] A sample of 2,2,3,3-tetramethylbutane was supplied through the kindness of Dr. Kenneth Greenlee of the Department of Chemistry of the Ohio State University. The nitric oxide used in this work was purchased from the Matheson Company, Inc., and certified as 99.0% pure. It was purified further by bulb-to-bulb distillation on the vacuum line. The material used condensed to a white solid. The isobutene and isobutane used in these experiments were Matheson Company C.P. grade, 99.0 % minimum and were used without further treatment.

Procedure for the Kinetics and Product Studies.—The reaction vessels used were spherical glass bulbs of 300 cc. nominal capacity. They were fitted with mercury manometers for the kinetic runs and with break-tips for runs in which product analyses were to be carried out. The volume exterior to the thermostat in the kinetic runs was of the order of 1–2 cc.

The bulbs were filled on a vacuum line. In most cases 2,2′-azoisobutane, at room temperature, was allowed to vaporize into the evacuated bulb until the vapor pressure, about 22 mm. was reached. The bulb contents were then condensed in the bulb bottom by means of a cold bath and the bulb sealed off with a torch. In larger scale experiments, a reservoir bulb of known volume was filled with 2,2′-azoisobutane at its vapor pressure, the contents transferred,

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[1] This research was supported by the United States Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command, under contract No. AF 49(638)-483. Reproduction in whole or in part is permitted for any purpose of the United States Government.

[2] E. Farenhorst and E. C. Kooyman, *Rec. trav. chim.*, **72**, 993 (1953).

by means of a cold trap, to the reaction bulb and the entire process repeated enough times to get the desired pressure. Mixtures of 2,2'-azoisobutane and nitric oxide or isobutene were prepared in a similar manner.

Results

The Products of the Reaction.—The products of the reaction consisted of gaseous products and of a brown solid deposit invariably observed on the walls. The ratio of the final to initial pressure was 2.40 ± 0.06 over the 180–220° temperature range studied. No trend with temperature was found.

Mass spectrographic analysis[3] of the products of the reaction revealed that isobutane and nitrogen were the main products comprising together more than 90% of the total products. 2,2,3,3-Tetramethylbutane was present in small amount. It was not possible to get accurate analyses for it because of the presence of small amounts of unknown materials, but the amount present was estimated as 5–10% that of the nitrogen. Isobutene was absent or was present in trace amounts only. In experiments where the products that would pass through a liquid nitrogen-cooled trap were examined, it was found that methane was present in amount 2–4 % that of the nitrogen. Qualitative examination of the infrared spectra of the products supported the above results.

To get further information on the products, experiments were carried out with amounts of 2,2'-azoisobutane corresponding to 10–15 times those used in the ordinary runs. The products were then fractionated by means of a Toepler pump and cold traps. The fraction passing through a series of liquid nitrogen-cooled traps was first collected. The fraction of the remainder that passed through a series of traps at −40° was collected next. The residue constituted the third fraction. From the amount of the first fraction, which was nitrogen and methane, and the mass spectrographic analysis, the amount of nitrogen formed was calculated. The results of the large scale experiments are shown in Table I and are in each case the average of four experiments, the average deviation being given.

TABLE I

THE PRODUCTS OF THE THERMAL DECOMPOSITION OF 2,2'-AZOISOBUTANE

	Nitrogen	Fraction passing −40° bath	Remainder
2,2'-Azoisobutane, mole/mole	1.02 ± 0.05	1.34 ± 0.09	0.09 ± 0.02

It is clear that one mole of nitrogen is formed per mole 2,2'-azoisobutane. In view of the mass spectrographic results, the second fraction is assumed to be isobutane and the third, 2,2,3,3-tetramethylbutane.

In one experiment on the above scale, an attempt was made to measure the amount of solid material on the walls. *n*-Hexane and trichloroethylene solvents were used in succession; the former removed much of the deposit and the latter a little more. It was estimated that 75–90 % of the wall deposit was recovered. The weight of brown solid found on evaporating the solvent corresponded to 14% by weight of the 2,2'-azoisobutane. When this figure was corrected for the estimated amount of undissolved material on the walls, the weight per cent yield became 16–19%.

The Kinetics of the Reaction.—The progress of the reaction was followed by measuring the change in pressure. Measurements were made at 180, 190 200, 205, 210 and 220°. The data gave good first order kinetics. The rate constants were calculated from the slopes and are estimated to be accurate to ± 5%. The temperature dependence of the rates is shown in Fig. 1 and corresponds to an activation energy of 42.8 kcal./mole and a frequency factor of 2.2 × 10^{16} sec.$^{-1}$.

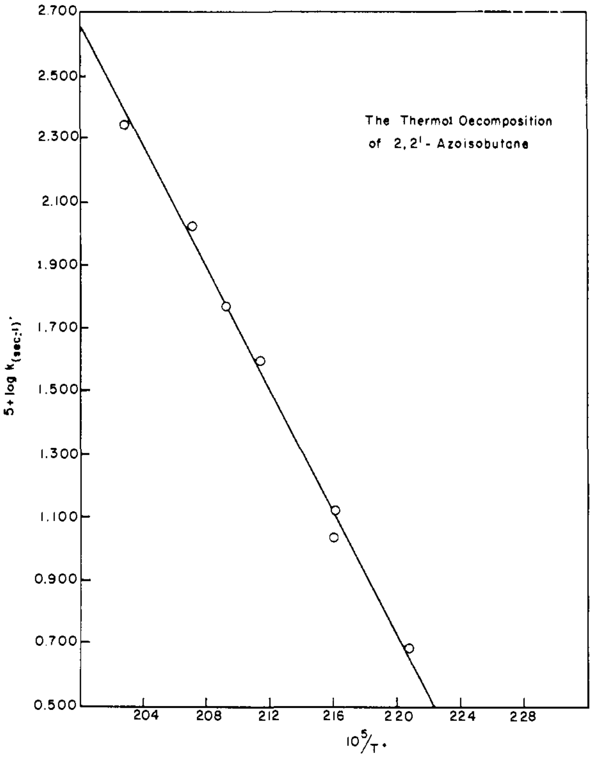

Fig. 1.

Experiments were carried out wherein the reaction was stopped by removing the bulbs from the bath and the amount of nitrogen that had been produced was measured by means of the cold trap-Toepler pump technique. Rates based on the nitrogen formed are shown in Table II.

It may be pointed out that the rates determined from the nitrogen measurements were, in effect, determined from a single data point and hence are not as reliable as the manometric data. The results of Table II confirm the validity of the manometric method for measuring the rates.

The effect of surface on the reaction rate was tested by packing a bulb with short lengths of 6 mm. Pyrex tubing. The ratio of surface area to volume was about 3 times that in the ordinary runs, but the rate constant was unaffected.

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[3] We are indebted to Dr. Robert G. Nugent of this Laboratory for the mass spectrographic analyses reported here.

Experiments with Added Isobutene.—Experiments were performed at 210° in which the thermal decomposition of 2,2′-azoisobutane was carried out in the presence of a two-fold excess of isobutene. In one experiment, manometric data were taken and at the end of the reaction the products were transferred to an infrared cell by a Toepler pump. Comparison of the product spectrum[4] with those of isobutene at known pressures showed that 70–80 % of the isobutene had been consumed. The spectrum was similar to that of the ordinary runs, indicating the formation of isobutane as the main products. Visual examination of the reaction bulb showed that very little solid, much less than in ordinary runs, had been formed. When the data were plotted for first order kinetics, the rate constant found was 1.19×10^{-3} sec.$^{-1}$, compared to the 1.07×10^{-3} sec.$^{-1}$ value found for 2,2′-azoisobutane alone at this temperature.

TABLE II

COMPARISON OF RATE DATA OBTAINED AT 190° MANOMETRICALLY AND BY NITROGEN DETERMINATION

Type measurement	Reaction, %	$10^5 k$ (sec.$^{-1}$)	Temp. (°C.)
Manometric	..	13.8	190
Nitrogen	33.5	14.1	190
Nitrogen	66.0	15.3	190
Manometric	..	4.98	180
Nitrogen	67.5	5.01	180

In other experiments with a two-fold excess of isobutene, the reaction was stopped before completion and the nitrogen that had formed was collected by the Toepler pump-cold trap technique. The rate constants so calculated agreed, within experimental error, with the rate found manometrically for 2,2′-azoisobutane alone.

TABLE III

THE THERMAL DECOMPOSITION OF 2,2′-AZOISOBUTANE IN THE PRESENCE OF ISOBUTENE AT 210°

Method measurement	Reaction, %	$10^3 k$ (sec.$^{-1}$)
Manometric	..	1.07
Nitrogen	20.8	1.18
Nitrogen	32.8	1.09
Nitrogen	57.1	1.11
Nitrogen	72.0	1.05

The rate of the thermal decomposition of 2,2′-azoisobutane was thus unaffected by the presence of twice its amount of isobutene.

Experiments with Added Nitric Oxide.—Kraus and Calvert[5] have reported that, in the presence of nitric oxide, the normal products of the photolysis of di-*t*-butyl ketone at 104.8° and 106.9°, isobutane and 2,2,3,3-tetramethyl-butane were absent while the yield of isobutene was doubled. They suggested that the reaction

$$(CH_3)_3C\cdot + NO \longrightarrow \text{iso-}C_4H_8 + HNO \qquad (a)$$

accounted for this. It would be expected that this reaction would be accompanied by

$$2HNO \longrightarrow N_2O + H_2O \qquad (b)$$

It thus appeared that the thermal decomposition of 2,2′-azoisobutane in the presence of nitric oxide would yield isobutene, nitrous oxide and water as products and a pressure increase equal to exactly twice the initial pressure of 2,2′azoisobutane.

Experiments were carried out over the 180–220° temperature range with 2,2′azoisobutane containing varying amounts of added nitric oxide. It was found that the pressure remained constant at its initial value for periods of time proportional to the amount of nitric oxide present. The pressure then began to increase. When the reaction bulb was examined, a blue vapor was observed, and when the products were passed through a liquid nitrogen-cooled trap, a blue liquid was observed.[5,6]

The above phenomena suggested that the reaction

$$(CH_3)C\cdot + NO \longrightarrow (CH_3)_3CNO \qquad (c)$$

was occurring and that the product was stable at these temperatures. Reaction rate constants calculated on this basis were in rough agreement with the manometric data. When experiments were carried out wherein more nitric oxide than required by equation c was present, it was observed that the pressure did not remain constant but began to increase after a time corresponding to about 70–80 % reaction as calculated from the rate data for 2,2′-azoisobutane alone. The infrared spectra of the products showed that isobutene and nitrous oxide were present. Peaks corresponding to the principal peaks of 2-methyl-2-nitrosopropane were observed at 6.35 and 7.30 μ.[7]

Discussion

The Mechanism of the Reaction.—It is evident from the results with nitric oxide that this reaction proceeds by a free radical mechanism and that no molecular decomposition occurs. In addition, the product analysis showed that all the nitrogen in the products was present as molecular nitrogen. Therefore, these steps are posulated

$$(CH_3)_3CN{=}NC(CH_3)_3 \xrightarrow{k_1} 2(CH_3)_3C\cdot + N_2 \qquad (1)$$

$$2(CH_3)_3C\cdot \xrightarrow{k_2} (CH_3)_3CC(CH_3)_3 \qquad (2)$$

$$2(CH_3)_3C\cdot \xrightarrow{k_3} \text{iso-}C_4H_8 + \text{iso-}C_4H_{10} \qquad (3)$$

The high isobutane yields and the absence of isobutene in the products require a step wherein isobutane is formed at the expense of isobutene. The experiments performed with 2,2′-azoisobutane–isobutene mixtures showed that isobutene was consumed, furnishing strong evidence for the reaction

$$(CH_3)_3C\cdot + \text{iso-}C_4H_8 \longrightarrow \text{iso-}C_4H_{10} + CH_2{=}C(CH_3)CH_2\cdot \qquad (4)$$

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[4] The infrared spectra referred to in this paper were taken on a Perkin-Elmer Infracord graciously made available to us by Mr. Max Tryon of the Rubber Section of the National Bureau of Standards.

(5) J. W. Kraus and J. G. Calvert, THIS JOURNAL, **79**, 5921 (1957).

(6) W. D. Emmons, *ibid.*, **79**, 6522 (1957).

(7) We are grateful to Dr. Charles B. Colburn for a copy of the infrared spectrum of this compound.

This reaction is analogous to that generally written to explain the inhibition of chain reactions by propylene, isobutene being even more reactive than propylene in this way.[8]

The fate of the rather stable allylic radical formed in reactions of this sort is generally assumed to be dimerization

$$2CH_2{=}C(CH_3)CH_2\cdot \longrightarrow CH_2{=}C(CH_3)CH_2CH_2(CH_3)C{=}CH_2 \quad (5)$$

Since the dimer also has the allylic structure, further reaction sequences like (4) and (5) can be written. These could be repeated until a high enough molecular weight was reached for the material to deposit on the walls. In the presence of added isobutene, reaction 4 would predominate over reactions with the higher molecular weight allylic hydrocarbons and the wall deposit would be reduced or eliminated.

It is possible to write the stoichiometry of the reaction if the reported value of 0.22[5] for the $k_2:k_3$ ratio is used and a formula for the wall deposit is assumed. As an example, the wall deposit may be assigned the formula $C_{32}H_{50}$. (It may be pointed out that the stoichiometry is hardly affected if formulas of $C_{16}H_{26}$ or $C_{64}H_{98}$ are chosen.) Each $C_{32}H_{50}$ corresponds to eight isobutene residues and twenty-two isobutane molecules (eight from disproportionation and fourteen from abstraction). The $k_2:k_3$ ratio of 0.22 requires the formation of 1.76 molecules of 2,2,3,3-tetramethylbutane per molecule of $C_{32}H_{50}$. The stoichiometry thus becomes

$$16.76(CH_3)_3CN{=}NC(CH_3)_3 \longrightarrow C_{32}H_{50} + 22 \text{ iso-}C_4H_{10} + 1.76(CH_3)_3CC(CH_3)_3 + 16.76\ N_2$$

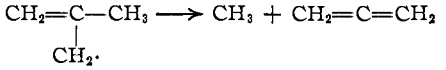
The above equation is consistent with the observed results in that (1) isobutene is absent; (2) the isobutane:nitrogen ratio of 1.31 is in good agreement with the 1.34 value observed; (3) the ratio of final to initial pressure, assuming $C_{32}H_{50}$ has a negligible vapor pressure, is 2.42, compared to 2.40 ± 0.06 observed; (4) the weight % yield of $C_{32}H_{50}$ in the above equation is 18, in agreement with the 16-19 weight % yield observed. The 10.5 % yield predicted in the equation for 2,2,3,3-tetramethylbutane is somewhat higher than the observed but not beyond the accuracy of the estimate.

It may be concluded that the results in the presence of added isobutene showed that no induced decomposition occurred. (Kraus and Calvert[5] observed a similar result with di-*t*-butyl-ketone up to 320°.) It is of some interest that abstraction by *t*-butyl radical occurs rapidly at these temperatures for the allylic hydrogen of isobutene but is apparently much slower for the hydrogen in 2,2′-azoisobutane. For methyl radical, abstraction from isobutene appears to occur only a little more readily than from azomethane.[8] The greater selectivity in the reactions of the less reactive radical, *i.e.*, *t*-butyl, as compared to methyl radical, is not unexpected.[9]

No explanation has been included in the above mechanism for the methane formation. Methyl radicals, which could subsequently abstract an allylic hydrogen to give methane, could be formed by

$$(CH_3)_3C\cdot \longrightarrow CH_2{=}CHCH_3 + CH_3\cdot$$

or[10]



$$CH_2{=}\underset{\displaystyle CH_2\cdot}{\underset{|}{C}}{-}CH_3 \longrightarrow CH_3 + CH_2{=}C{=}CH_2$$

Propene would be consumed in a manner similar to that of isobutene while allene would undoubtedly polymerize. In any event, the amount of methane formed was very small and it is not believed that its formation could have affected the main course of the reaction.

The Kinetics of the Reaction.—The rate constant measured for this reaction corresponds to k_1, since step 1 is the only step in which 2,2′-azoisobutane is consumed. The concordance of the manometric rates and those calculated from the nitrogen formed, Table II, confirms the validity of the manometric method. It is of interest to show that the validity of the method is consistent with the mechanism. The method requires that products be formed in constant proportions throughout the reaction. The kinetics are complicated by the fact that the *t*-butyl radical reacts with the various species C_4H_8, C_8H_{14}, $C_{16}H_{26}$, etc. It seems plausible that these reactions would be fast until the hydrocarbon species reached a high enough value to be deposited on the walls, in which form their reactivities could well be negligibly small. If, with this assumption, the steady state approximation is made for C_4H_8, C_8H_{14}, etc., it is easy to show that the rate of formation of every product, except nitrogen, is proportional to $((CH_3)_3C\cdot)$.[2] The products would thus be formed in constant proportions throughout the experiment, fulfilling the requirement for validity of the manometric method.

TABLE IV

THE THERMAL DECOMPOSITION OF AZOALKANES

Compound	A (sec.$^{-1}$)	ΔS^*[11] e. u.	E^* (kcal./mole)	$k_{250°}$ (sec.$^{-1}$)	Relative rate at 250°
Azomethane[12]	3.13×10^{15}	15.8	52.5	3.5×10^{-6}	1
Azoethane[13]	5.87×10^{14}	12.5	48.5	3.0×10^{-5}	8.6
Methyl isopropyl diimide[14]	2.8×10^{14}	11.0	47.5	3.8×10^{-5}	10.9
Azoisopropane[15]	5.6×10^{12}	3.3	40.9	4.4×10^{-4}	125
2,2-Azoisobutane	2.2×10^{15}	15.2	42.8	2.8×10^{-2}	8000

The kinetic parameters for 2,2′-azoisobutane are compared with those of the other azoalkanes in Table IV. The data for the other azoalkanes all refer to the rates at high pressures, *i.e.*, pressures above those at which rate dependence on total pressure is observed. Although the kinetics of the

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[8] A. F. Trotman-Dickenson, "Gas Kinetics," Academic Press, Inc., New York, N. Y., 1955, p. 200.

[9] J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1956, p. 431.

[10] We are grateful to one of the referees for pointing out this possibility.

[11] $\Delta S^* = 2.303\ R \log A/1.09 \times 10^{13}$ at 250°.

[12] H. C. Ramsperger, THIS JOURNAL, **49**, 912 (1927).

[13] D. F. Swinehart, private communication.

[14] H. C. Ramsperger, THIS JOURNAL, **51**, 2134 (1929).

[15] H. C. Ramsperger, *ibid.*, **50**, 714 (1928).

thermal decomposition of 2,2'-azoisobutane were not studied as a function of pressure, it is believed that the working pressures involved were in the high pressure region. This belief is based on: (a) the fact that 2,2'-azoisobutane is a complex enough molecule so that it should have exhibited first order kinetics at even lower pressures than those used[16]; (b) the fact that the addition of isobutene in amounts twice that of the 2,2'-azoisobutane did not affect the rate.

The kinetic data for azomethane have been questioned on the grounds that chain reaction contributions to the rate must be considered.[17] Steel and Trotman-Dickenson[18] have recently found some evidence for a chain contribution to the rate but found that the fully inhibited reaction yielded a frequency factor of $10^{15.7}$ sec.$^{-1}$ and an activation energy of 51.2 kcal./mole, in good agreement with the data of Ramsperger quoted above. Swinehart[14] has reported that azomethane, azoethane and azoisopropane decomposed with no sign of a chain reaction. It seems safe to assume that the data quoted in Table IV apply to the initial rupture of the molecule in all cases.

The effect of structure on reactivity can be examined by comparing activation energies or relative rates at a given temperature. If the former standard is used, it is seen that replacing methyl groups by ethyl, isopropyl and *t*-butyl groups results in a decrease in the activation energy. The observed order of effectiveness in lowering the activation energy, isopropyl > *t*-butyl > ethyl > methyl is anomalous, however, since it would be expected that *t*-butyl would be more effective than isopropyl.[19] Both the frequency factor and activation energy for azoisopropane are anomalously low and imply a difference in its transition state which distinguishes it from methyl isopropyl diimide and 2,2'-azoisobutane. Such a difference is difficult to explain. Since the frequency factors for all the azoalkanes but azoisopropane are of the order of 10^{15}–10^{16} sec.$^{-1}$, it seems that a comparison on the basis of identical frequency factors, *i.e.*, comparison of rate constants at a given temperature, would be more reliable. This comparison, for a temperature of 250°, is shown in Table IV and places the order of effectiveness in increasing the reaction rate, as *t*-butyl > isopropyl > ethyl > methyl, a more reasonable order. It may be pointed out that the rather large entropies of activation found, 11.0–15.8 cal. mole^{-1} deg.$^{-1}$, are consistent with the general picture of this reaction as the simultaneous breakdown of the azoalkane to two alkyl radicals and nitrogen.[20] Such a process might well be expected to have a higher entropy of activation than a simple bond cleavage.

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(16) S. W. Benson, "The Foundations of Chemical Kinetics," McGraw-Hill Book Co., Inc., New York, N. Y., 1960, p. 234.

(17) M. Page, H. O. Pritchard and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 13878 (1953).

(18) C. Steel and A. F. Trotman-Dickenson, *ibid.*, **1959**, 975 (1959).

(19) S. G. Cohen and C. H. Wang, THIS JOURNAL, **77**, 2457 (1955).

(20) Ref. 9, page 423.