Thermolysis of Azoalkanes in a Stirred-flow System

By **G. Martin,*** Centre of Petroleum and Chemistry, Instituto Venezolano de Investigaciones Científicas, Apartado 1827, Caracas, Venezuela
Allan Maccoll, Christopher Ingold Laboratories, University College London, 20 Gordon Street, London WC1H 0AJ.

The gas-phase thermal decomposition of azoethane, ethaneazo-1′-methylethane, and azo-2′-methylpropane have been investigated in a stirred-flow system using the toluene carrier technique. The order of the reaction for the disappearance of the azoalkanes has been found to be nearly unity in each case. The temperature dependence of the rate coefficients is given by the Arrhenius equations: azoethane, $\log k = 14.2 \pm 0.2 - (186 \pm 2\ \text{kJ mol}^{-1})/2.30RT$; ethaneazo-1′-methylethane, $\log k = 16.5 \pm 0.5 - (206 \pm 3\ \text{kJ mol}^{-1})/2.30RT$, and azo-2′-methylpropane, $\log k = 15.6 \pm 0.3 - (170 \pm 3\ \text{kJ mol}^{-1})/2.30RT$. No evidence was found for hydrogen atom abstraction by alkyl radicals from the toluene carrier. An average value of 0.14 ± 0.03 was obtained for the disproportionation : combination ratio of the ethyl radicals in the temperature range 280—400 °C. For the t-butyl radicals this ratio had a value of 2.9 ± 0.2 between 210 and 260 °C.

THE pyrolyses of azoethane (AE) and azo-2′-methylpropane (AMP) [1-8] prompted us to study the gas phase thermolysis of ethaneazo-1′-methylethane (EAM) in order to compare the results obtained for AE and other asymmetrical and symmetrical azoalkanes.[9] The present work has been carried out in a stirred-flow system with the reactant previously diluted in a stream of carrier gas such as toluene or carbon dioxide in an attempt to avoid the complications due to secondary reactions experienced by previous workers and also to assess the effectiveness of toluene in preventing hydrogen atom abstraction by the free alkyl radicals from the azo-compound. In the case of AE, the rate coefficient for hydrogen atom abstraction from the parent compound by ethyl radical has been given [10] as $k = 10^{11.4}\exp(-33.5 \pm 0.8\ \text{kJ mol}^{-1}/RT)\ \text{cm}^3\ \text{mol}^{-1}\ \text{s}^{-1}$ between 27 and 175 °C. The rate coefficient for hydrogen abstraction from toluene by ethyl has been reported [11] as $k = 10^{10.9}\exp(-39 \pm 8\ \text{kJ mol}^{-1}/RT)\ \text{cm}^3\ \text{mol}^{-1}\ \text{s}^{-1}$ in the range 328—400 °C. For methyl radicals, the value for the latter reaction is considered well established; one measurement [12] made using the stirred-flow technique gave the equation $k = 10^{11.4}\exp(-38 \pm 1\ \text{kJ mol}^{-1}/RT)\ \text{cm}^3\ \text{mol}^{-1}\ \text{s}^{-1}$ between 159 and 270 °C. On the basis of the above parameters, these reactions could be expected to be nearly competitive or, if the concentration of toluene is kept much higher than that of the azo-compound, abstraction from the carrier gas should be favoured.

RESULTS AND DISCUSSION

Thermolysis of AE.—The runs were carried out at temperatures in the range 280—400 °C and total pressures between 3 and 13 Torr. In Table 1 are collected the analytical results and experimental conditions of some of the runs in which a complete product analysis was attempted. The formation of C_2H_6 seems to be favoured by long residence times, small degrees of conversion, and low temperatures as can be inferred from the data between 271 and 340 °C. The ratio $C_2H_4 : C_4H_{10}$, which gives the disproportionation : combination ratio ($k_d : k_c$) of ethyl radicals, had an average value of 0.14 ± 0.03. This average was obtained including runs not shown in Table 1. The material balance

---

[1] W. D. Clark, D. F. Swinehart, and R. D. McCoy, Abstracts, 132nd National Meeting of the American Chem. Soc., New York, 1957, p. 475.

[2] H. S. Sandhu, *J. Phys. Chem.*, 1968, **72**, 1857.

[3] O. P. Strausz, R. E. Berkley, and H. E. Gunning, *Canad. J. Chem.*, 1969, **47**, 3470.

[4] J. B. Levy and B. K. W. Copeland, *J. Amer. Chem. Soc.*, 1960, **82**, 5314.

[5] D. F. McMillen, D. M. Golden, and S. W. Benson, *J. Amer. Chem. Soc.*, 1972, **94**, 4403.

[6] A. U. Blackhan and N. L. Eatough, *J. Amer. Chem. Soc.*, 1962, **84**, 2922.

[7] M. J. Perona, P. C. Beadle, and D. M. Golden, *Internat. J. Chem. Kinetics*, 1973, 495.

[8] S. W. Benson and H. E. O'Neal, 'Kinetic Data on Unimolecular Reactions,' NSRDS–NBS 21, 1970, U.S. Dept. of Commerce.

[9] R. J. Crawford and K. Takagi, *J. Amer. Chem. Soc.*, 1972, **94**, 7406.

[10] 'Tables of Bimolecular Gas Reactions,' A. F. Trotman-Dickenson and G. S. Milne, NSRDS–NBS, 1967, U.S. Dept of Commerce.

[11] A. C. Lalonde and S. J. W. Price, *Canad. J. Chem.*, 1971, **49**, 3367.

[12] M. F. R. Mulcahy, D. J. Williams, and J. R. Wilmshurst, *Austral. J. Chem.*, 1964, **17**, 1329.

of the products, expressed by the ratio $C:N$ was in most cases within 10% of the theoretical value 2.0. No visible material remained in the system after completing the study of this compound.

In Table 1, the columns headed ' AE out N ' and ' AE out g.l.c.' give the amounts of unchanged AE calculated by subtraction of moles of N_2 collected from the input moles of reactant and the amount measured by g.l.c., respectively. The discrepancy between these two values was in many cases as high as 10% but the estimation based on the nitrogen measurement can be considered more accurate on experimental grounds.

TABLE 1

Reaction product composition and experimental conditions for AE

		10^8Flow (mol s^{-1})				10^4AE out g.l.c.	10^4AE out N	10^4 Total product	% of total							
t/°C	p/Torr	f°_{A} [a]	f_C [a]	f_{N_2} [a]	Reaction (%)	(mol) [b]	(mol) [b]	(mol)	N_2	CH_4	C_2H_6	C_2H_4	C_3H_8	C_3H_6	n-C_4H_{10}	10^4k/s^{-1}
273.1	11.38	106		1.13	1.1		37.7	102	38.8	1.5	46.1	4.3	0.9	1.4	7.9	1.68
284.1	12.79	164	2.8	3.06	1.9	26.8	28.9	124	44.5	1.0	32.5	2.5	0.7	0.6	19.6	4.99
309.6 *	8.55	103	271	3.87	3.8	17.8	17.8	144	48.3	0.8	17.1	3.9	1.6	0.7	33.9	30.8
340.9	9.15	75.6	3 231	2.34	3.1	13.3	13.2	86.9	48.5	0.2	22.4	5.0	0.5	0.2	24.0	215
339.3	12.12	45.6	1 275	4.48	9.8		8.64	209	44.9	0.2	19.0	3.7	0.4	0.1	32.1	222
339.4	2.75	107		21.1	19.7		15.4	785	48.3	0.3	13.6	3.2	0.9	0.5	33.3	234
337.9	7.51	103	186	22.3	21.7	13.9	14.5	830	48.4	0.2	13.7	3.1	0.9	0.5	33.1	223
383.5	11.6	67.9	6 613	9.53	14.0	10.9	10.5	322	53.3	0.2	12.9	4.9	0.3	0.1	31.0	2 164
395.2	9.07	70.9	4 926	19.9	28.0	10.5	9.19	698	51.3	0.1	14.3	4.9	0.5	0.1	30.5	4 383
402.5	10.04	104	5 410	34.9	33.7	13.6	12.4	1 257	50.1	0.1	13.8	3.9	0.4	0.0	32.1	5 787

* Carbon dioxide used as carrier gas.

[a] f°_{A} = Inflow of reactant, f_C = flow of carrier gas, f_{N_2} = outflow of nitrogen. [b] See text.

The order of the reaction for the disappearance of AE was found to be 1.13 ± 0.06 at 340 and 1.16 ± 0.03 at 328 °C which agree with the previously reported[2] 1.2 ± 0.1 at 271.5 °C.

Analysis of liquid effluent from runs made in the absence of carrier gas showed the presence of products of molecular weight higher than AE. The semi-quantitative analysis of these products shown below was obtained assuming equal response of the g.l.c. detector for all the peaks eluted.

TABLE 2

Analysis of secondary products. Temperature 340 °C, conversion 56%, unreacted AE 11.94 × 10^{-4} mol, secondary products 1.18 × 10^{-4} mol

Product	10^4 Amount (mol)	Gas products	10^4 Amount (mol)	
Ethanal diethylhydrazone	0.27	N_2	15.19	$C:N$ 1.6
Ethaneazo-1′-methylpropane	0.13	n-C_4H_{10}	9.24	
$C_{10}H_{21}N_3$	0.21	C_2H_6	5.27	
$C_8H_{17}N_3$	0.10	C_2H_4	1.26	
Mixture *	0.10			
Unidentified (total)	0.34			
			10^4 Amount (mol)	
		Total C_2H_6 released	30.4	
		Total C_2H_5 in gas	25.0	

* Probably ethanal diethylhydrazone and ethaneazo-1-methylpropane.

. Formation of ethanal diethylhydrazone and ethaneazo-1′-methylpropane has been reported previously[3] together with some ethanal ethylhydrazone. Two peaks of m/e 155 and 183 whose fragmentation patterns suggest that they belong to compounds containing three nitrogen atoms and two double bonds are represented by the formulae $C_8H_{17}N_3$ and $C_{10}H_{21}N_3$ respectively. No evidence at all was found for hydrogen atom abstraction by ethyl from toluene. The mass spectrum of the gaseous hydrocarbon products from a run made at 340 °C and 27% conversion using fully deuteriated toluene failed to reveal any deuteriated ethane; however, it can be easily estimated by means of reported Arrhenius parameters[10-12] and steady state concentrations of reactants, that *ca.* 12% of the ethane should be converted into C_2H_5D for this particular run. For runs made using normal toluene, most of the C_2H_6 should come from abstraction from $PhCH_3$ at the higher temperatures. No bibenzyl or aromatic compounds other than toluene and its impurities were detected in the liquid effluent of the runs even at the highest temperature studied. The conclusion arrived at in connection with these experiments is that hydrogen abstraction from AE by ethyl takes place much more readily than extrapolation of the reported Arrhenius equation for this process suggests, so that abstraction from toluene is not competitive at all with it. In fact, the system could be better described as AE itself behaving as carrier gas.

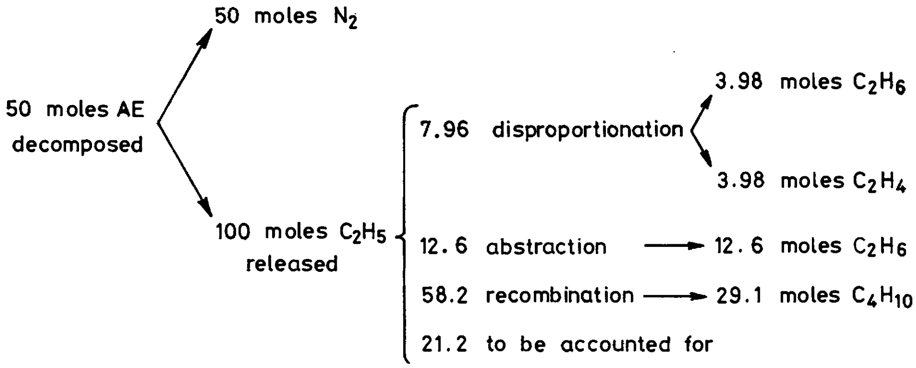
The values of rate coefficients for hydrogen abstraction by ethyl from AE that we estimated from the present experiments showed some dependence on the conditions of each run. They increased at low percentage conversion and in the temperature range 380—400 °C they were definitely one power of ten higher than those calculated using the reported Arrhenius parameters.[10]

The two most important features of the thermolysis of AE are the large excess of C_2H_6 over C_2H_4 and the constancy of the ratio $C_2H_4:C_4H_{10}$ over the whole temperature range. An overall equation for the decomposition of AE into the main products can be obtained by averaging the percentage of each product for runs done between 310 and 402 °C. This averaging yielded the stoicheiometry (A) from which the ratios

$$50C_2H_5N{=}NC_2H_5 \longrightarrow 49.8N_2 + 16.6C_2H_6 + 3.98C_2H_4 + 29.1C_4H_{10} + 0.5(C_1 + C_3) \quad \text{(A)}$$

$C_2H_4:C_4H_{10} = 0.136$ and $C_2H_6:C_2H_4 = 4.17$ are obtained. Assuming that for each molecule of nitrogen formed two ethyl radicals are released, Scheme 1 should hold for the modes of reaction of the ethyl radicals.

According to Scheme 1 *ca.* 21 moles of C_2H_5 and 12.6 moles of hydrogen deficient AE molecules remain unaccounted for. Only those products of molecular weight higher than AE can be used to account for the ' missing ' C_2H_5 and of these compound $C_{10}H_{21}N_3$ can be assumed to provide three, the one of formula $C_8H_{17}N_3$ two, ethaneazo-1′-methylpropane and ethanal diethylhydrazone one ethyl each in excess of the two ethyl groups forming one AE molecule. In the analysis shown above these contributions reduce the amount of unaccounted ethyl to 4.2×10^{-4} mole and raise the ratio $C : N$ to 1.7. The ethyl still unaccounted for would be represented by the unidentified products assuming they provide a total of *ca.* 10 C_2H_5.



SCHEME 1

The sequence of reactions proposed in Scheme 2 to explain the results of the present thermolysis of AE in the stirred-flow system is similar to those reported previously for thermal [2,3] and photolytic [13] decompositions of this reactant. Each particular step proposed has been considered the most likely on account of its known activation energy and availability of the species involved in the reaction.

$C_2H_5N{=}NC_2H_5 \longrightarrow C_2H_5 + N{=}NC_2H_5$ (1a)
$C_2H_5N{=}N \longrightarrow C_2H_5 + N_2$ (1b)
$2C_2H_5 \longrightarrow C_2H_4 + C_2H_6$ (2)
$2C_2H_5 \longrightarrow C_4H_{10}$ (3)
$C_2H_5 + AE \longrightarrow C_2H_6 + CH_3CHN{=}NCH_2{-}CH_3\ (AE^{\bullet})$ (4)
$C_2H_5 + C_4H_{10} \longrightarrow C_2H_6 + C_4H_9$ (5)
$C_4H_9 \longrightarrow CH_3 + C_3H_6$ (6)
$CH_3 + C_2H_5 \longrightarrow C_3H_8$ (7)
$CH_3 + AE \longrightarrow CH_4 + AE^{\bullet}$ (8)
$C_2H_5 + AE^{\bullet} \longrightarrow CH_3CH{=}NN(C_2H_5)_2$ (9)
$C_2H_5 + AE^{\bullet} \longrightarrow C_4H_9N{=}NC_2H_5$ (10)
$AE^{\bullet} + AE \longrightarrow$ Products (11)

SCHEME 2

Formation of methane implies the presence of methyl radicals in the system. Reaction (6) has been reported [8] to have a rate coefficient given by the equation $k = 10^{14.16}\exp(-142\ \text{kJ mol}^{-1}/RT)$, and hence it is considered here to be the most likely source of methyl. The necessary s-butyl radicals can originate from reaction (5), which is a low activation energy process whose Arrhenius parameters have been reported [14] as $k = 10^{13.9\pm0.4}\exp(-92 \pm 8\ \text{kJ mol}^{-1}/RT)\ \text{cm}^3\ \text{mol}^{-1}\ \text{s}^{-1}$.

The presence of ethaneazo-1′-methylpropane suggests that this compound can be expected to have an activation energy for decomposition of about the same magnitude or higher than AE; an estimate using the method of group contributions [8,15] gives E_a 197 ± 13 kJ mol^{-1} for the former reaction assuming initial s-butyl splitting. Since AE is one of the most abundant species in the system, reactions (4) and (8) must be very much favoured. The $k_d : k_c$ ratio for CH_3 and C_2H_5 has a value of *ca.* 0.04 [10] which favours reaction (7). The main source of C_2H_6 besides reaction (2) has to be reaction (4) since the two most abundant species, C_2H_5 and AE, intervene in it. The amount of C_2H_6 formed by reaction (5) cannot be very significant, about as much as C_1 or C_3 products, for any large variation in the production of n-butane would be reflected in the ratio $k_d : k_c$ of the ethyl radicals and this has been found to remain fairly constant. The complexity of the products in the pyrolysis of AE is presumably due to the radical $AE^{\bullet}$ being stable and formed in high concentration. As has been suggested before,[2,3] some resonance stabilization can be expected by way of the structures $CH_3\dot{C}HN{=}NCH_2CH_3 \longleftrightarrow CH_3CH{=}N{-}\dot{N}CH_2CH_3$. These would yield by combination with an ethyl radical ethaneazo-1′-methylpropane and ethanal diethylhydrazone. This radical could also combine with AE to yield heavier nitrogen-containing products. In the non-inhibited thermolysis of azomethane [16] the formation of species which can be considered the homologues of those formed from AE was reported. Their origin was also thought to be the radical $CH_3N_2CH_2$ which is stabilized by resonance and available for combination reactions.

The decomposition of the alternative unstabilized AE

---

[13] H. Cerfontain and K. O. Kutschke, *Canad. J. Chem.*, 1958, **36**, 344.

[14] D. G. Hughes, R. M. Marshall, and J. H. Purnell, *J.C.S. Faraday I*, 1974, 594.

[15] P. S. Engel, J. L. Wood, J. A. Sweet, and J. L. Margrave, *J. Amer. Chem. Soc.*, 1974, **96**, 2381.

[16] Y. Paquin and W. Forst, *Internat. J. Chem. Kinetics*, 1973, 691.

radical taking place in any large extent according to reaction (12) would be very difficult to reconcile with the

$$CH_2CH_2N{=}NC_2H_5 \longrightarrow C_2H_4 + N_2 + C_2H_5 \quad (12)$$

constancy of the ratio $C_2H_4 : C_4H_{10}$ since this extra source of ethylene would raise its value. This fact hints at the negligible formation of such radical.

Thermolysis of EAM.—Table 3 shows the analytical results of some of the runs carried out with this compound between 260 and 320 °C and pressures in the range 3—13 Torr. The *C* : *N* material balance of the products was in nearly all cases below the theoretical value 2.50, although within 10% of this figure. To ensure the collection of C_5 hydrocarbon in the liquid phase, it was necessary to carry out product fractionation at −110 °C. This caused a substantial amount of butane to remain dissolved and this had to be accounted for afterwards in the analysis of the liquid fraction. This procedure, however, always yielded low estimates due to loss of butane during handling of the sample. The low figure for the amount of C_4 products formed is reflected as well in the cross-combination ratio for the ethyl and isopropyl radicals obtained according to the relation $C_5 : (C_4 \times C_6)^{1/2}$. The value of this ratio given by the geometric mean rule[17] is very close to 2.0, the weighted average obtained in this work being 2.2 ± 0.2. The two minor products, methane and isobutane, are probably formed in about the same amount, although it was not determined how much of the C_4 product dissolved in the liquid phase was isobutane.

TABLE 3

Reaction product composition and experimental conditions for EAM

t/°C	p/Torr	Flow (mol s^{-1}) $f°_A$	f_c	f_{N_2}	Reaction (%)	10^4EAM out g.l.c. (mol)	10^4EAM out N (mol)	10^6 Total product (mol)	% of total N_2	CH_4	C_2H_6	C_2H_4	C_3H_8	C_3H_6	i-C_4H_{10}	n-C_4H_{10}	i-C_5H_{12}	C_6H_{14}	10^4k/s^{-1}
260.3	11.21	96.7	97.01	0.72	0.7	17.36	17.27	32.40	39.1	0.9	18.3	2.4	15.2	6.6	0.2	4.1	9.7	4.6	2.11
269.8	9.59	33.4	46.14	1.07	3.2	8.93	8.73	71.80	39.6	0.7	17.4	3.0	14.4	8.6	0.1	2.7	8.7	4.7	4.62
280.4	11.93	26.8	158.1	1.05	3.9	7.06	6.97	64.30	43.3	0.6	14.0	2.9	11.0	7.5	0.1	4.4	10.6	5.6	10.64
290.8	8.06	27.8	17.88	4.59	16	6.75	6.28	303	40.2	0.6	21.8	5.6	4.6	3.3	0.3	5.6	12.3	5.8	21.70
300.7	8.35	91.8	109.3	10.9	12	15.09	14.59	455	42.6	0.4	9.6	2.8	10.1	7.9	0.2	5.6	14.3	6.5	60.16
310.4	12.13	25.9	345.7	4.35	17	6.41	5.84	268	43.6	0.3	10.0	2.8	9.9	8.2	0.1	5.8	13.2	6.4	116.6
320.0	11.58	29.8	1 967	1.93	6.5	7.82	7.51	130	39.9	0.3	17.7	3.8	10.8	7.8	0.1	4.8	9.9	4.9	215.4

The order of the reaction for the disappearance of EAM was determined at 301, 310, and 320 °C yielding the values 0.99 ± 0.07, 0.88 ± 0.99, and 1.19 ± 0.07 respectively, which indicate an overall order very close to unity.

The thermolysis of EAM can be represented by a sequence of steps similar to that used in the case of AE, having only to include the cross-combination and cross-disproportionation reactions of ethyl and isopropyl as well as hydrogen abstraction from two preferential sites in the EID molecule. The latter would give rise to radicals (I) and (II). Radical (II), being formed at a

$$CH_3\dot{C}H\text{-}N{=}NCH(CH_3)_2 \longleftrightarrow CH_3CH{=}N\text{-}\dot{N}CH(CH_3)_2 \quad (I)$$

$$CH_3CH_2N{=}N\dot{C}(CH_3)_2 \longleftrightarrow CH_3CH_2\dot{N}\text{-}N{=}C(CH_3)_2 \quad (II)$$

secondary carbon atom, is probably somewhat more stable than (I). Also both can be expected to be more stable than the radical formed from the similar AE molecule. An estimate was made of the apparent activation energies (E_{app}) for the formation of the main hydrocarbon products from EAM, on the basis of the variation of their rate of production with the temperature. A least square Arrhenius fit of these data yielded the values shown in Table 4.

The importance of a second path for the formation of C_2H_6 and C_3H_8 which is hydrogen abstraction by the radicals from the parent compound is reflected as a lower E_{app} for these products. The figure for ethane compares well with a similar estimate of E_{app} for C_2H_6 from AE, which yields a value of 133 ± 4 kJ mol^{-1}. In the same way as previously, a run was made at 290 °C and 10% conversion using [$^2H_8$]toluene as carrier gas and the C_2—C_5 hydrocarbon fraction was analysed by mass spectrometry. The intensity of the peaks of *m*/*e* 45 and 31 did not differ from that of a product sample obtained using normal toluene. This evidence together with the absence of other aromatics ruled out the possibility of hydrogen abstraction from $PhCH_3$ in any substantial amount.

Thermolysis of AMP.—The mechanism of the thermolysis of AMP in a stirred-flow system implies exclusively the recombination and disproportionation of t-butyl radicals formed in the initial bond fission step as inferred from the results shown in Table 5. The reaction yields nearly constantly 37% of nitrogen, 27% each of isobutane and isobutene, and 9% of 2,2′,3,3′-tetramethylbutane, with an average stoicheiometry of 2.68 ± 0.07 product molecules formed from each molecule of reactant decomposed. The *C* : *N* material balance of the products was in every case within 5% of the theoretical value 4.0. There was also very good agreement between the calculated and the measured amount of unchanged material. The average value of the $k_d : k_c$ ratio for the

TABLE 4

Product	E_{app}/kJmol^{-1}
C_5H_{12}	210 ± 4
n-C_4H_{10}	208 ± 4
C_6H_{14}	203 ± 4
C_3H_6	197 ± 8
C_2H_4	195 ± 8
C_3H_8	167 ± 8
C_2H_6	154 ± 8

---

[17] J. O. Terry and J. H. Futrell, *Canad. J. Chem.*, 1967, **25**, 2327.

t-butyl radicals was obtained as 2.9 ± 0.2 or 2.7 ± 0.2 depending on whether isobutane or isobutene is used in the relation $C_4 : C_8$.

The order of the reaction for the disappearance of AMP was obtained as 1.089 ± 0.002 at 231, 1.10 ± 0.07 at 240, and 1.12 ± 0.02 at 260 °C for conversions between 6 and 30% which suggest a first-order process.

The pyrolysis of AMP in a static system[4,5] is rather complicated, in particular hydrogen abstraction from isobutene by t-butyl radicals causes a nearly total consumption of this product with the formation of isobutane and allylic radicals which polymerize to form a solid deposit on the walls of the reaction vessel. It has been considered[5] that this hydrogen abstraction is competitive with disproportionation and recombination of the t-butyl radicals; however, the results of the present work are contrary to such assumption. In view of the above results, it appears that of the three azoalkanes studied in the present work, the thermolysis of AMP was the only case in which the flow system technique produced the desired result of a simpler reaction scheme.

TABLE 5

Reaction product composition and experimental conditions for AMP

		10^8 Flow (mol s^{-1})				10^3AMP out g.l.c.	10^4 AMP out N	10^4 Total product	% of total				
t/°C	p/Torr	$f°_A$	f_c	f_{N_2}	Reaction (%)	(mol)	(mol)	(mol)	N_2	$i\text{-}C_4H_{10}$	$i\text{-}C_4H_8$	C_8H_{18}	10^4k/ s^{-1}
210.5	11.21	64.0	51.6	6.39	10.0	15.67	15.56	4.70	36.7	27.5	26.1	9.8	18.67
220.4	11.76	32.0	106	5.76	18.0	9.38	9.44	5.67	36.6	27.7	26.1	9.6	41.73
230.9	11.49	68.6	338	10.6	15.4	12.59	12.54	6.21	36.7	26.3	26.3	9.2	103.8
239.5	11.59	82.2	313	22.8	27.7	13.04	13.19	13.72	36.9	27.2	26.0	9.8	227.6
259.7	8.78	82.7	1 372	22.5	27.2	10.99	10.84	10.94	37.0	26.5	26.9	9.6	1 032

The Arrhenius Parameters of the Azoalkanes.—A 95% confidence limit, least-square computer program was employed to calculate the Arrhenius parameters from the experimental kinetic data of the three azoalkanes. The resulting equations were (13)—(15).

AE

$$\log k = 14.2 \pm 0.1 - \frac{(186 \pm 2)\ \text{J mol}^{-1}}{2.303RT} \qquad (13)$$

EAM

$$\log k = 16.5 \pm 0.3 - \frac{(206 \pm 3)\ \text{J mol}^{-1}}{2.303RT} \qquad (14)$$

AMP

$$\log k = 15.6 \pm 0.3 - \frac{(170 \pm 3)\ \text{J mol}^{-1}}{2.303RT} \qquad (15)$$

In Table 6 are collected the Arrhenius parameters for AE and AMP taken from recent literature together with those obtained in the present work. The rate coefficient calculated at three widely separated temperatures as well as the Arrhenius parameters and rate coefficients corresponding to EAM are included for comparison. For the case of AE, these figures show that although the present Arrhenius parameters are lower than all the other values reported, the rate coefficients are in general in good agreement with those calculated from literature data. The largest discrepancies occur with the values provided by parameters III and V which are Benson and O'Neal's[8] preferred values and the parameters favoured by Perona *et al.*[7] The latter authors found that parameters IV would also agree with their RRKM treatment of the experimental data but favoured V for being closer to Benson and O'Neal's values.

In their assessment of the reliability of the experimental data for bond fissions, Benson and O'Neal pointed out that the Arrhenius parameters obtained by the toluene carrier technique are usually low due to the fact that in some cases there is a chain-stimulated decomposition promoted by free radicals which toluene does not inhibit. We tried to interpret our low Arrhenius parameters in the light of the above argument considering a low E_a path for the production of nitrogen which would be a short chain comprising reactions (4) and (12) of the sequence as propagating steps. Reaction (12) is the most obvious second path for the production of nitrogen although we already gave a reason to consider it improbable. Taking reaction (12) into account, this yields the absolute rate of formation of nitrogen as equation (16). The steady state concentration of

$$d[N_2]/dt = k_1[AE] + k_{12}[C_2H_4N_2C_2H_5] \qquad (16)$$

radicals AE$^{\bullet}$ can be considered to be given mainly by

TABLE 6

Parameter	log A	E_a/ kJ mol^{-1}	AE 10^4k (280 °C)/ s^{-1}	10^2k (340 °C)/ s^{-1}	$10k$ (400 °C)/ s^{-1}	Ref.
I	15.7	203	3.4	2.6	9.0	1
II	15.1	197	2.9	1.9	6.2	2
III	16.3	209	3.5	3.0	11.7	8
IV	15.4	200	3.8	2.3	7.6	7
V	16.4	208	5.8	4.8	18.4	7
VI	14.2	186	3.8	2.0	5.2	This work
			EAM			
	16.5	206	11.0	8.6	31.7	This work
			AMP 10^3k (210 °C)/ s^{-1}	10^2k (240 °C)/ s^{-1}	10^2k (260 °C)/ s^{-1}	
I	16.3	179	1.2	1.6	7.7	4
II	17.15	180	4.6	6.3	31.0	6
III	17.15	182	3.0	9.4	21.0	8
IV	16.6	182	0.8	1.2	5.9	7
V	16.4	179	1.1	1.5	7.2	7
VI	15.6	170	1.8	2.1	9.4	This work

(17), assuming $k_{12} \gg k_4$. Substitution of (17) into (16)

$$[AE^{\bullet}] = k_4[AE][C_2H_5]/k_{12} \qquad (17)$$

yields (18). The second term of the right hand side of

$$d[N_2]/dt = k_1[AE] + k_4[AE][C_2H_5] \qquad (18)$$

(18) can be interpreted as the low activation energy path for the production of nitrogen. Comparison of (18) with the rate equation (19) for C_2H_6 indicates that the

$$d[C_2H_6]/dt = k_2[C_2H_5]^2 + k_4[C_2H_5][AE] \qquad (19)$$

amout of 'secondary' nitrogen provided by this path should be equal to the amount of ethane formed by reaction (4). To assess the effect of these assumptions on the rate coefficients and Arrhenius parameters for AE, the rate coefficients were calculated again using as effluent flow rate of nitrogen f'_{N_2} given by $f'_{N_2} = f_{N_2}\text{-}\ (f_{C_2H_6} - f_{C_2H_4})$. A least-square treatment of the data for the linear Arrhenius plot yielded equation (20).

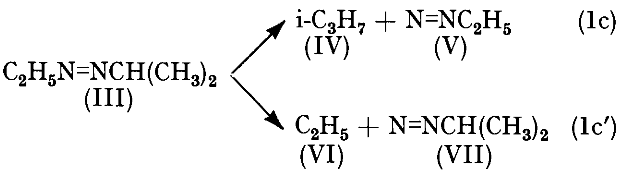
$$\log k = 14.55 \pm 0.7 - \frac{(204 \pm 8)\ \text{kJ mol}^{-1}}{2.30RT} \qquad (20)$$

Although the above parameters are closer to the literature values, the rate coefficients obtained on the basis of the above corrections are lower than those obtained by using any of the parameters of Table 6:

t/°C	280	340	400
k/s^{-1}	1.7×10^{-4}	1.3×10^{-2}	4.5×10^{-1}

These values are rather unrealistic as compared to those in Table 6. On the basis of better agreement with reported rate coefficients the parameters $E_a = 186 \pm 2$ kJ mol^{-1} and $\log A = 14.2 \pm 0.2$ should be considered more reliable than those of equation (20). Accepting that our Arrhenius parameters for AE are definitely low, it is worth noting that those for EAM have the 'expected' high values. If there was any influence of the experimental technique on the kinetic parameters, they should have been affected the same way in both cases. On the other hand, the high values for EAM would suggest the absence of any chain or radical induced decomposition as assumed earlier in the case of AE. This would indicate that the radical EAM$^{\bullet}$ is indeed very stable and does not decompose easily to provide a low E_a path for the production of nitrogen.

The results of Crawford and his co-workers [9] on the pyrolysis of selected symmetrical and unsymmetrical azo-compounds together with the thermochemical calculations of Benson and O'Neal give firm support to the view that the initial step of the decomposition is best represented by reactions such as (1a and b) and not by simultaneous two-bond fission. If the initial step takes place according to (1a), then the measured E_a can be identified with the C–N bond dissociation energy. Two paths (1c and c') can be considered for the initial step of the decomposition of EAM. Using Benson and O'Neal's method of group additivities and the latest



$$C_2H_5N{=}NCH(CH_3)_2\ \text{(III)} \rightarrow i\text{-}C_3H_7\ \text{(IV)} + N{=}NC_2H_5\ \text{(V)} \qquad (1c)$$

$$C_2H_5N{=}NCH(CH_3)_2\ \text{(III)} \rightarrow C_2H_5\ \text{(VI)} + N{=}NCH(CH_3)_2\ \text{(VII)} \qquad (1c')$$

estimations of group values made by Engel *et al.*[15] the following $\Delta H_f°$ values can be calculated for species (III)—(VII):

	(III)	(IV)	(V)	(VI)	(VII)
$\Delta H_f°$/kJ mol^{-1} (± 4)	65	73	188	109	159

These values give $\Delta H°(1c) = 197 \pm 12$ and $\Delta H°(1c') = 205 \pm 12$ kJ mol^{-1}. Path (1c) is favoured by *ca.* 8 kJ mol^{-1}. The experimental value of E_a (206 ± 3 kJ mol^{-1}) is within the calculated $\Delta H°$ values although if path (1c) is favoured the E_a for EAM should be expected to be closer to that for azo-1-methylethane than to that for AE, *i.e.* 197 kJ mol^{-1}.[8]

The figures shown in Table 6 for AMP indicate that the rate coefficients of this work are somewhat higher than all the others, excluding parameters II and III which appear to be the less reliable. It does not seem reasonable to suppose that in the present experiments a chain process took place which produced nitrogen *via* a low E_a path. The simplicity of the reaction product distribution is not indicative of complex radical reactions and the possibility of hot radical induced decomposition does not seem probable either with the reaction taking place in the presence of a concentration of $PhCH_3$ higher than that of the reactant. It can be expected that if the toluene is not acting as radical inhibitor, at least it should be effective as moderator in stabilizing hot radicals by energy transfer.

EXPERIMENTAL

AE was prepared by the method of Renaud and Leitch.[18] EAM was prepared as described by Spialter *et al.*[19] AMP was obtained in 50% yield by the method of Stevens [20] and purified by eluting the crude product through a 60 cm long column packed with Woelm alumina grade III. The lighter impurities were eluted first with isopentane and AMP was then eluted with diethyl ether. The purity of the azo-compounds was checked by g.l.c., n.m.r., and mass spectrometry and shown to be >99.8%. AnalaR toluene (Fison) was used as carrier gas. G.l.c. analysis, on a 10 ft column packed with 20% Apiezon L grease on 60—80 mesh Chromosorb P at 170 °C and 30 lb in^{-2} nitrogen input pressure, showed the presence of two impurities of retention times equal to those of isopropyl- and s-butyl-benzene. Since these impurities were present only in amounts of *ca.* 0.1% and blank runs showed that no gases were evolved in measurable quantities, toluene was used without further purification.

The vacuum system used was similar to the conventional toluene carrier flow system developed originally by Szwarc [21] but incorporating the modifications of Mulcahy

---

[18] R. Reanaud and L. Leitch, *Canad. J. Chem.*, 1954, **32**, 545.

[19] L. Spialter, D. H. O'Brian, G. L. Untereiner, and W. A. Rush, *J. Org. Chem.*, 1965, **30**, 3278.

[20] T. E. Stevens, *J. Org. Chem.*, 1961, **26**, 2531.

[21] M. Szwarc, *Chem. Rev.*, 1950, **47**, 75, and references therein.

and Williams.[22] The reaction vessel was in principle similar to that of the latter authors, except that its shape was that of a cylinder with spherical ends with length 14 cm and 5 cm outer diameter. The internal sphere, of 2.6 cm outer diameter, was placed 2.8 cm from the bottom. The total volume of the reactor, including internal and connecting tubing maintained at the same temperature as the main cylinder, was 205 cm^3. Two Pt–Pt 13% Rh thermocouples, placed at the centre of the internal sphere and at the exit of the reactor, were used to read the temperature. The readings from these thermocouples never differed by more than 0.2 °C.

The rate coefficients for the reaction were obtained from the rate of production of nitrogen calculated using the Mulcahy and Williams [22] equation.

The order of the reaction for the disappearance of the azo-compound was determined by a method similar to that described by Graaf and Kwart,[23] from plots of log $(f_A^\circ - f_A)$ against log $(f_A/\Sigma f_i)$, where f_A° and f_A are the influent and effluent flow rates of azo-compound and Σf_i the total effluent flow rate. The slope of the straight line obtained in each plot corresponds to the order of the reaction.

C_1—C_4 Hydrocarbons were analysed on a 4 m × 1/8 in, 100—120 mesh activated alumina column between 50 and 90 °C. The liquid fraction was analysed in an 8 ft × 1/8 in column packed with 20% dinonyl phthalate on 60—80 mesh G-cell between 40 and 60 °C. The column used to search for the presence of bibenzyl was a 1 m × 1/8 in 20% silicone gum rubber on Supasorb 40—60 mesh at 120 °C and 15 lb in^{-2} nitrogen input pressure. The analysis of the nitrogen-containing secondary products from the pyrolysis of AE was carried out in a PYE 104 gas chromatograph coupled to a MS30 double beam mass spectrometer. The column used was 5 ft × 0.25 in (glass) 10% polyethylene glycol 20M on Celite 100—120 mesh, between 100 and 120 °C with helium at 40 ml min^{-1}. The hydrocarbons and starting materials were determined quantitatively using an internal standard on a Perkin-Elmer F11 gas chromatograph fitted with a flame ionization detector.

[6/1340 *Received*, *9th July*, 1976]

[22] M. F. R. Mulcahy and D. J. Williams, *Austral. J. Chem.*, 1961, **14**, 534.

[23] J. de Graf and H. Kwart, *J. Phys. Chem.*, 1963, **67**, 1458.