Combination and Disproportionation Reactions of the $CH_3CH - N - NC_2H_5$ Radical

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The radical $CH_3CH - N - NC_2H_5$ (1) was produced in the di*tert*-butyl peroxide-initiated and thermal decompositions of azoethane. Self-combination of 1 takes place almost exclusively at the carbon radical centre (1C). The disproportionation: combination ratio $\Delta(\dot{C}_2H_5, 1N) \approx 0.38$ ($\Delta = k_d/k_c$) and the rate constant ratio $k_d(\dot{C}H_3, 1N)/k_c(\dot{C}H_3, 1C) = 0.15 \pm 0.03$. The cross-combination ratio $\phi(\dot{C}H_3, 1C) = 1.38 \pm 0.11$, which is lower than the cross-reaction ratio $\phi^*(\dot{C}H_3, 1) \approx 2.5$.

One of the kinetically significant radicals in both the photolytic and thermal reactions of azo compounds is the substituted diazaallyl radical, whose stabilization energy is similar to that of the allyl radical.^{1,2} It is formed in radical H-atom abstraction from the parent azo compound, *e.g.* in the case of azoethane (AE):

 $\mathbf{R} + \mathbf{CH}_{3}\mathbf{CH}_{2}\mathbf{N} = \mathbf{NCH}_{2}\mathbf{CH}_{3} \rightarrow$

$$\mathbf{RH} + \mathbf{CH}_{3}\mathbf{CH} - \mathbf{N} - \mathbf{NCH}_{2}\mathbf{CH}_{3} \quad (1)$$

No detailed experimental work has been reported on further reactions of diazaallyl radicals. The only products identified are formed in cross-combinations with alkyl radicals.^{3–5} Formation of *syn*- and *anti*-acetaldehyde ethylhydrazone was observed both in gas-phase H-atom abstractions and/or disproportionations of 1 and in the surface-catalysed tautomerization of AE to hydrazones.^{3,6}

Gray and Thynne⁷ have tentatively identified the dimer of 2,3-diazabutenyl radical in the thermal decomposition of azomethane, but no quantitative kinetic data are available so far on the self-combinations and disproportionations of such radicals. The self-combination products of 1 are expected to be less stable than the parent azo compound; thus, secondary decompositions are expected to occur in photolytic and thermal reactions. Since decomposition can be avoided at lower temperatures, in an attempt to obtain quantitative kinetic data on some bimolecular reactions of 1, experiments were carried out on the di-*tert*-butyl peroxide (DTBP)-initiated thermal reaction of AE. The thermally initiated reaction of AE alone was also studied.

Experimental

The DTBP-initiated gas-phase decomposition of AE was studied in the concentration ranges $1.0 < [AE]_0/10^{-3}$ mol dm⁻³ < 3.3 and $0.9 < [DTBP]_0/10^{-4}$ mol dm⁻³ < 4.2 at 397–444 K. The thermal decomposition of AE alone was investigated at a concentration of 1.6×10^{-3} mol dm⁻³ at 509–564 K. The maximum conversions of DTBP and AE were 20% and 2%, respectively, in the initiated decomposition, and 15% in the decomposition of 'pure' AE. The typical conversions were half of these values.

AE was synthetized by the method of Renaud and Leitch⁸ and purified by gas chromatography. Its purity was better than 99.5 mol%. DTBP was purchased from Fluka AG. It was washed with water, dried over anhydrous Na_2SO_4 , distilled *in vacuo* and stored in a dark vessel.

The experiments were carried out in a static reactor. The cylindrical reactor was made of quartz. Greaseless (PTFE) stopcocks were used. The pressure was measured by a BHL

4400-10 pressure transducer (Transamerica Instruments). The sampling line was heated to 380 K.

Two samples were made from the reaction mixture.

Gaseous sample: ca. half of the reaction mixture was expanded through the heated sample line to a cylindrical sampling vessel (containing a small amount of *n*-pentane as a standard) equipped with a PTFE valve. The analyses were performed by expansion of the contents of this bulb, heated to prevent separation by condensation, through a heated connecting tubing to the heated gas sampling valve of the GC.

Liquid sample: the rest of the reaction mixture was frozen rapidly into a small bulb with a cold finger (*ca.* 83 K) which contained a standard dissolved in nonane. This sample was injected directly into the heated inlet splitter of the GC with a 10^{-5} dm³ Hamilton syringe.

The hydrocarbon products were separated on a Durapak/ *n*-octane on Porasil C (3 m, 3.2 mm diameter) column, and the N- and O-containing products from the liquid sample on an HP OV 101 Carbowax deactivated FSOT column (50 m). A Hewlett Packard 5734 gas chromatograph equipped with a flame-ionization detector was used. The products were identified by using the pure substances and/or by mass spectrometry (VG Micromass 12F1A GC/MS). References to the methods used for the identification of different products as well as the abbreviations used are included in Tables 1 and 2.

We assume that the elution sequence of the diastereoisomers of 5,6-dimethyl-3,4,7,8-tetraazadeca-3,7-diene

 Table 1
 Product distribution of the methyl radical-initiated decomposition of AE;^a methods of identification

product	mol%	methods
CH ₄	17.73	b
$C_2 H_6$	7.63	b
C_2H_4	0.60	b
C_3H_8	0.62	b
C_3H_6	0.02	b
iso-C ₄ H ₁₀	0.15	b
$C_{4}H_{10}$	0.01	b
acetone	56.67	b, c
tert-butyl alcohol	0.96	b, c
$C_2H_3N = NCH(CH_3)_2$ (EMED)	3.26	b, c
$CH_3CH = NN = CHCH_3 (AEH)$	0.83	b, c
$C_2H_5N(H)N(CH_3)C_2H_5$	2.25	с
$syn-CH_3CH=NN(H)C_2H_5$	0.04	b, c
anti-CH ₃ CH=NN(H)C ₂ H ₅	0.02	b, c
$CH_3CH = NN(CH_3)C_2H_5$ (AEMH)	4.16	с
$C_2H_5(CH_3)N(CH_3)C_2H_5$ (DEDMH)	4.06	С
$meso-C_2H_5N=NCH(CH_3)CH(CH_3)N=NC_2H_5$	0.47	с
(\pm) -C ₂ H ₅ N=NCH(CH ₃)CH(CH ₃)N=NC ₂ H ₅	0.52	с

^a T = 429 K, $[DTBP]_0 = 0.18 \times 10^{-3}$ mol dm⁻³, $[AE]_0 = 1.67 \times 10^{-3}$ mol dm⁻³. ^b Authentic sample. ^c GC/MS.

 Table 2
 Product distribution in the thermal decomposition of AE,^a

 methods of identification

product	mol%	methods
CH	2.57	b
$C_3 H_6$	60.24	b
$C_{2}H_{4}$	2.54	b
C ₁ H ₈	0.37	b
C ₁ H ₆	0.16	b
$\tilde{C_4H_{10}}$	7.84	b
1-C ₄ H ₈	0.08	b
(E)-but-2-ene	0.48	b
(Z)-but-2-ene	0.14	b
3-methylpentane	0.17	b, c
CH ₃ CH=NN=CHCH ₃ (AEH)	3.06	b, c
$C_2H_5N = NCH(CH_3)C_2H_5$ (EMPD)	12.30	с
$CH_3CH = NN(C_2H_5)_2$ (ADEH)	7.66	b, c
$meso-C_2H_5N=NCH(CH_3)CH(CH_3)N=NC_2H_5$	1.08	с
(\pm) - C_2H_5N =NCH(CH ₃)CH(CH ₃)N=NC ₂ H ₅	1.31	с

^a T = 544 K, $[AE]_0 = 1.6 \times 10^{-3}$ mol dm⁻³. ^bAuthentic sample. ^c GC/MS.

 $(C_8H_{18}N_4)$, bisazo compound) is the same as those of a structurally analogous compound (3,4-dimethylhexa-1,5-diene), where the *meso* isomer is eluted first.⁹ The retention indices extrapolated to 323 K are: $I(meso-C_8H_{18}N_4) = 1024$, $I[(\pm)-C_8H_{18}N_4] = 1034$.

In the DTBP-initiated reaction we have also analysed unidentified compounds with retention indices 70–90 index units (i.u.) higher than those of the bisazo compounds with good reproducibility. The sum of their peak areas was similar to the sum of those of ethyl (1-methylethyl)diazene (EMED) and acetaldehyde ethylmethylhydrazone (AEMH).

In the thermal decomposition of AE, no products with elution times higher than those of the bisazo compounds were observed in greater than negligible amounts. Formation of products with smaller elution times (boiling points) was observed in minor amounts.

The concentrations of the products were calculated on the basis of the effective carbon number concept.^{10,11} For determination of the unknown FID response factor, some diazenes,¹² hydrazones and hydrazines were synthesized or purchased and analysed on the above column; the amounts

injected for the calibration were similar to those in the sample.

The reported errors in the kinetic data obtained are standard deviations.

Results and Discussion

Typical product distributions of the DTBP-initiated and thermal decompositions of AE are presented in Tables 1 and 2, respectively.

The elementary reactions yielding the dominant radicals and products in the DTBP-initiated reaction are shown in Scheme 1, and those of the thermal decomposition of AE in Scheme 2. The theoretical expressions for the formation of the different products are based on these schemes.

Self-combination of $CH_3CH - N - NC_2H_5$

The only self-combination products (bisazo compounds) observed are formed in the combination at the C-atom radical centre (1C) [reaction (13), (A6)]. The 1C-1N and 1N-1N hydrazone-type combination products are expected to be more stable than the bisazo compounds. In spite of this, no characteristic fragments of these products were observed in the mass spectra. Thus, formation of such combination products in higher than negligible amounts can be excluded. This conclusion is in agreement with earlier observations^{13,14} on the combinations of different substituted diazaallyl radicals.

The ratios of the initial rates of formation of the *meso-* and (\pm) -C₈H₁₈N₄ isomers are practically independent of the temperature and composition of the reaction mixture in both the initiated and the thermal decompositions:

$$\frac{r_{meso}}{r_{(\pm)}} = 0.90 \pm 0.07(397-444 \text{ K})$$
$$\frac{r_{meso}}{r_{(\pm)}} = 0.87 \pm 0.07(507-563 \text{ K})$$

Since secondary decomposition of these isomers is significant in the thermal decomposition, but negligible in the DTBP-initiated reaction, the stabilities of the two isomers are

$(CH_3)_3COOC(CH_3)_3 \rightarrow 2(CH_3)_3CO$	(1)
$(CH_3)_3C\dot{O} \rightarrow \dot{C}H_3 + (CH_3)_2C = O$	(2)
$2 \text{ CH}_3 \rightarrow \text{C}_2\text{H}_6$	(3)
$\dot{C}H_3 + C_2H_5N = NC_2H_5 \rightarrow CH_4 + CH_3CH - N - NC_2H_5$	(4)
$\dot{C}H_3 + C_2H_5N = NC_2H_5 \rightarrow C_2H_5\dot{N}N(CH_3)C_2H_5$	(5)
$\dot{C}H_3 + CH_3\dot{C}HN = NC_2H_5 \rightarrow 2-C_3H_7N = NC_2H_5$	(6)
$\dot{C}H_3 + CH_3CH = N\dot{N}C_2H_5 \rightarrow CH_3CH = NN(CH_3)C_2H_5$	(7)
$\dot{C}H_3 + CH_3\dot{C}H = NNC_2H_5 \rightarrow CH_4 + CH_3CH = NN = CHCH_3$	(8)
$C_2H_5\dot{N}N(CH_3)C_2H_5 + 1N \rightarrow C_2H_5N(H)N(CH_3)C_2H_5 + CH_3CH=NN=CHCH_3$	(9)
$\dot{C}H_3 + C_2H_5\dot{N}N(CH_3)C_2H_5 \rightarrow CH_4 + CH_3CH = NN(CH_3)C_2H_5$	(10)
$2 C_2 H_5 \dot{N}N(CH_3)C_2 H_5 \rightarrow C_2 H_5 N(H)N(CH_3)C_2 H_5 + CH_3 CH = NN(CH_3)C_2 H_5$	(11)
$\dot{C}H_3 + C_2H_5\dot{N}N(CH_3)C_2H_5 \rightarrow C_2H_5N(CH_3)N(CH_3)C_2H_5$	(12)
2 CH ₃ CHN=NC ₂ H ₅ \rightarrow meso-, (±)-C ₈ H ₁₈ N ₄	(13)
$2 C_2 H_5 \rightarrow C_4 H_{10}$	(14)
$\dot{C}_2H_5 + C_2H_5N = NC_2H_5 \rightarrow C_2H_6 + CH_3CH - N - NC_2H_5$	(15)
Scheme 1 Reduced mechanism of the DTBP-initiated decomposition of AE	

J. CHEM. SOC. FARADAY TRANS., 1991, VOL. 87

$$C_2H_5N = NC_2H_5 \rightarrow 2\dot{C}_2H_5 + N_2 \tag{A1}$$

$$C_2H_5 + C_2H_5N = NC_2H_5 \rightarrow C_2H_6 + CH_3CH - N - NC_2H_5$$
(A2)

$$\dot{C}_{2}H_{5} + CH_{3}\dot{C}HN = NC_{2}H_{5} \rightarrow C_{2}H_{5}CH(CH_{3})N = NC_{2}H_{5}$$

$$\dot{C}_{3}H_{4} + CH_{3}CH = N\dot{N}C_{3}H_{4} \rightarrow CH_{3}CH = NN(C_{3}H_{3})C_{3}H_{4}$$
(A3)

$$\hat{C} H = C H = N \hat{N} C H =$$

$$C_{2}n_{5} + Cn_{3}Cn - NNC_{2}n_{5} \rightarrow C_{2}n_{6} + Cn_{3}Cn - NN - ChCH_{3}$$
(A5)

$$2 \operatorname{CH}_{3} \operatorname{CHN} = \operatorname{NC}_{2} \operatorname{H}_{5} \to \operatorname{meso-}, (\pm) - \operatorname{C}_{8} \operatorname{H}_{18} \operatorname{N}_{4}$$
(A6)

$$2 \operatorname{C_2H}_5 \to \operatorname{C_4H}_{10}$$

similar. The difference of the isomer ratio from the expected value of unity is probably due to some impurity present in the peak of the (\pm) -isomer.

Cross-disproportionation of $CH_3CH - N - NC_2H_5$ with **Alkyl Radicals**

The ratio $\Delta(=k_d/k_c)$ for the disproportionation-combination reactions of \dot{C}_2H_5 and 1N yielding acetaldehyde ethylidenehydrazone (AEH), ethane and acetaldehyde diethylhydrazone (ADEH), respectively, can be estimated from the present data.

The major source of AEH formation is reaction (A5). Selfdisproportionation of 1 and possible contributions by oligomeric radicals can be ruled out, since otherwise the ratio r_{AEH}/r_{ADEH} would vary with temperature owing to the appearance of further terms (dependent on rate ratios, which in turn change with temperature) in the expression of r_{AEH}/r_{ADEH} .

The contribution of possible disproportionations of the 1,2-diethyl-1-ethylhydrazyl radical to the formation of ADEH can also be neglected, as formation of 1,2-diethyl-1-ethylhydrazine (a possible H-atom abstraction and selfdisproportionation product of the 1,2-diethyl-1-ethylhydrazyl radical) was not observed, indicating a very low stationary concentration of this radical.

 r_{AEH}/r_{ADEH} was estimated to be 0.38 \pm 0.03, and thus

$$\Delta(\dot{C}_{2}H_{5}, 1N) = \frac{k_{d}(C_{2}H_{5}, 1N)}{k_{c}(\dot{C}_{2}H_{5}, 1N)} \approx 0.38$$

 Δ (CH₃, 1N) cannot be determined directly by similar estimation in the initiated decomposition, since the CH_3 and 1Ncross-combination product AEMH is formed in disproportionation reactions (10) and (11) also. This difficulty can be circumvented, however, and $\Delta(\dot{C}H_3, 1N)$ can be estimated indirectly.

The rate of formation of AEH can be expressed (Scheme 1) as

$$r_{\text{AEH}} = k_8[CH_3][1] + k_9[C_2H_5NN(CH_3)C_2H_5][1]$$

The radical concentrations can be eliminated via the combination products [C₂H₆, EMED, and 1,2-diethyl-1,2dimethylhydrazine (DEDMH)], and after rearrangement we obtain the two-parameter equation

$$\frac{r_{AEH}}{r_{EMED}} = \frac{k_8}{k_6} + \frac{k_9 k_3}{k_6 k_{12}} \frac{r_{DEDMH}}{r_{C_2 H_6}}$$
(1)

The formation of a small amount of butane was observed in the initiated reaction. We found it reasonable to assume that ethyl radicals are formed in the initiated reaction also. In the calculation of the ratio $r_{\text{DEDMH}}/r_{C_2H_6}$, the amount of ethane formed in H-atom abstraction from AE by the ethyl radical (5-15% of the total amount) was subtracted by using the known rate coefficient of reaction (15) determined at temperatures below the usual range of thermal decomposition.¹⁵

Least-squares treatment of the data yields (see also Fig. 1)

.

$$k_{\rm d}$$
(CH₃, 1N)/ $k_{\rm c}$ (CH₃, 1C) = $k_{\rm g}/k_{\rm 6}$ = 0.15 ± 0.03
 $k_{\rm g}k_{\rm 3}/k_{\rm 6}k_{\rm 12}$ = 0.23 ± 0.03

In the thermal decomposition of 'pure' AE, ethyl(1-methylpropyl)diazene (EMPD) and ADEH are the products of combination reactions (A3) and (A4). r_{ADEH}/r_{EMPD} is independent of temperature and is equal to 0.63 ± 0.04 , so that $k_c(C_2H_5)$, $1N)/k_{c}(\dot{C}_{2}H_{5}, 1C) \approx 0.63.$

ADEH and EMPD are not expected to decompose noticeably at the low conversions applied, although they exhibit some decomposition at higher conversions (see the concentration vs. time curves⁵). A somewhat higher value of $k_{A4}/k_{A3} = 0.77$ has been reported.⁵

Assuming identical regioselectivities for the radicals \dot{C}_2H_5 and CH₃:

$$k_{\rm c}(\dot{\rm CH}_3, 1N)/k_{\rm c}(\dot{\rm CH}_3, 1C)$$

$$\approx k_{\rm c}(\dot{\rm C}_{2}{\rm H}_{5}, 1{\rm N})/k_{\rm c}(\dot{\rm C}_{2}{\rm H}_{5}, 1{\rm C}) \approx 0.63$$

we estimate that $\Delta(\dot{C}H_3, 1N) \approx 0.24$.

Alkyl radicals are known to have low reactivities in selfand cross-disproportionation reactions with substituted allyl radicals as compared to the similar reactions of alkyl-alkyl disproportionations.^{16,17} The higher values of $\Delta(\dot{\mathbf{R}}, \mathbf{1N})$ than those of alkyl-allyl disproportionations may be a consequence of the low reactivity of 1 in combinations.



(A7)

Application of the Geometric Mean rule to the Combination of $\dot{C}H_3$ and $CH_3CH - N - NCH_2CH_3$

According to collision theory, the cross-combination ratio ϕ is expected to be greater than 2 with increasing differences in the mass and collision diameter of the radicals.^{18,19} However, several experimental rate constants for radical cross-reactions have recently been shown to differ from the predicted values.²⁰ For the radicals $\dot{C}H_3$ and 1C

$$\phi(\dot{C}H_3, \mathbf{1C}) = \frac{r_{EMED}}{r_{C_2H_6}^{1/2}r_{C_8H_14N_4}^{1/2}} = 1.38 \pm 0.11$$

Only a very small temperature dependence of ϕ ($E = 2.8 \pm 1.2 \text{ kJ mol}^{-1}$) was observed.

For calculation of the cross-reaction ratio ϕ^* we have to take into account all of the cross- and self-combination and disproportionation products of $1:^{21}$

$$\phi^{*}(\dot{C}H_{3}, 1) = \frac{r_{EMED} + r_{AEM} + r_{AEH}}{r_{C_{2}H_{6}}^{1/2} (r_{1C-1C} + r_{1C-1N} + r_{1N-1N})^{1/2}}$$

By neglecting the very small contribution of the selfcombination product of 1C-1N and 1N-1N in the denominator, we obtain

$$\phi^{*}(\dot{C}H_{3}, 1) = \frac{r_{\text{EMED}}(1 + 0.63 + 0.15)}{r_{C_{2}H_{6}}^{1/2}r_{C_{8}H_{18}N_{4}}^{1/2}} \approx 2.5$$

The cross-combination ratio calculated for \dot{C}_2H_5 and 1C in the thermal decomposition of AE yields a value in excess of 3, indicating secondary decomposition of the self-combination product of 1C.

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