Thermal Reaction of the Isopropyl Radical with 2,3-Dimethylbut-2-ene

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The CH₃CHCH₃ radical (iP') initiated homogeneous gas-phase thermal reaction of 2,3-dimethylbut-2-ene has been studied at 490-540 K by means of the thermal decomposition of azoisopropane (AIP). The products were identified using gas chromatography (GC) and gas chromatography-mass spectrometry (GC-MS).

The rate constant for the decomposition of AIP:

$$AIP \rightarrow 2 CH_3 \dot{C}HCH_3 + N_2 \tag{1}$$

is $\log(k_1/s^{-1}) = (16.36 \pm 0.49) - (201.5 \pm 5.4)$ kJ mol⁻¹/ θ , where $\theta = RT \ln 10$.

The rate constant of the H-abstraction yielding the 1,1,2-trimethylallyl radical (TMA') relative to the corresponding self-combination was determined for the first time:

$$CH_{3}\dot{C}HCH_{3} + (CH_{3})_{2}C = C(CH_{3})_{2} \rightarrow C_{3}H_{8} + (CH_{3})_{2}C = C(CH_{3})\dot{C}H_{2}$$
(2)

$$CH_{3}\dot{C}HCH_{3} + CH_{3}\dot{C}HCH_{3} \rightarrow (CH_{3})_{2}CHCH(CH_{3})_{2}$$
(9)

 $\log[(k_2/k_9^{1/2})/dm^{3/2} \text{ mol}^{-1/2} \text{ s}^{-1/2}] = (4.99 \pm 0.49) - (57.0 \pm 5.4) \text{ kJ mol}^{-1}/\theta$. The TMA' formed in reaction (2) combines with iP' terminally and non-terminally. The ratio of the rate constants was found to be independent of temperature: $k_{10}/k_{11} = 2.8 \pm 0.1$. iP' disproportionates with both iP' and TMA'. The disproportionationcombination ratios determined are Δ (iP', iP') = 0.58 \pm 0.06 and Δ (iP', TMA') = 0.03 \pm 0.01.

Elementary reaction rate constants of homogeneous gasphase radical reactions are needed in the kinetic models developed to describe the complex reactions involved in oxidation, atmospheric chemistry and the establishment of structure-reactivity correlations, etc. Such data for the reactions of bulky hydrocarbons and radicals are rather scarce in the literature.

The thermal decomposition of azoisopropane (AIP) has been studied in the gas phase by many authors¹⁻⁶ with the aim of establishing the mechanism of the elementary decomposition reaction (synchronous or asynchronous, see ref. 7) and the Arrhenius parameters of the decomposition. Recently, Ács et al.^{8,9} proposed a detailed mechanism for the decomposition up to 1% conversion at 498-563 K.

The combination and disproportionation reactions of the 1,1,2-trimethylallyl radical (TMA') were investigated by Montague¹⁰ and by Baulch et al.¹¹ The rate constant ratio of the combination of the isopropyl radical (iP') and TMA' in the terminal and non-terminal positions was found to be 8 ± 2 . The disproportionation-combination ratio for some alkyl radicals and TMA[•] was determined to be 0.01.¹⁰⁻¹²

Quantitative data on the H-abstraction rate constants of iP' with alkenes have been reported only for propene.9,13

The aim of this work was to obtain relative rate constants for some of the reactions encountered when AIP is decomposed in the presence of 2,3-dimethylbut-2-ene (DMB2).

Experimental

Materials

The iP' source, AIP, was synthesized by means of the Renaud and Leitch method,¹⁴ its purity was better than 99.0 mol%. After bulb-to-bulb vacuum distillation it was stored in a dark vessel. DMB2, purchased from Fluka AG., contained 0.19% 2-methylbutane on purification.

The solvent, isooctane (Fluka AG., 99.65%), and the internal standards, n-undecane (Fluka AG., 99.5%) and n-pentane (Carlo Erba, 99.65%), were thoroughly degassed before use.

Apparatus and Procedure

The reactions were carried out in a conventional, all-Pyrex, grease-free, static high-vacuum system fitted with glass/Teflon stopcocks (J. Young Ltd.). A quartz reaction vessel (0.139 dm³) with a surface: volume ratio of 0.11 dm⁻¹ was used. Prior to the reactions, the system was evacuated to below 2×10^{-3} Pa. Pressure measurements were performed with a precision Texas Instruments Pressure Gauge (Type 145-01). The temperature of the reaction vessel was kept constant within ± 1 K over the range 480-540 K, and within ± 0.5 K during a run.

In order to ensure perfect mixing, the reactants were stored at 323 K in a mixing vessel for 1 h prior to admission into the reaction vessel. Two samples were taken for the analysis. The reaction mixture was expanded into a gas-sampling bulb (ca. 100 cm³) containing *n*-pentane as internal standard and the rest of the mixture was frozen into a solution of n-undecane as internal standard in isooctane. The connecting tubing of the sampling line was heated to ca. 380 K by means of a heating tape.

Two to five experiments were carried out under the same initial conditions, but for different reaction times in the early stages of the reaction to obtain data for determination of the rates of formation of products $(r_{prod.})$. In order to compensate for the narrow temperature range imposed by the thermal initiation method, the reactions were studied at 30 different experimental conditions.

Analysis

Qualitative analysis of the products was performed by GC methods, with reference compounds, and by GC-MS (HP GC-MSD: HP 5890A GC, HP 5970 MS, HP 9000/300 computer, MS Chemstation HP 59970C software). Quantitative analysis of the products was performed on gas and liquid samples with HP 5734A and HP 5750 GCs equipped with a flame ionization detector. Different columns were used for the analyses: (i) Separation of the C_1-C_5 fraction was performed with a 3 m (3.2 mm diameter) stainless-steel column filled with Durapak-*n*-octane/Porasil-C and with a 50 m OV-101 fused silica capillary column (Hewlett-Packard). (ii) Separation of the C_5-C_{13} fraction was carried out on the liquid samples with the same OV-101 column, using temperature programming.

On the basis of the results of Sternberg *et al.*,¹⁵ the detector responses of alkanes and alkenes were assumed to be proportional to the effective carbon number (proportional to 1 per alkane and 0.95 per alkene carbon atom).

The formation of products was predicted by a simple, straightforward mechanism of the reaction (Scheme 1) prior to the experimental work.

Results and Discussion

Products of the Reaction

The identified products and the product compositions obtained in two typical reactions are shown in Table 1. The

initial rates of the products for the first eight experimental sets are shown in Table 2. (The data for the further 22 experimental conditions are published as supplementary material.[†])

The paraffin: alkene ratio (β) was estimated for all the products except the products of alkyl-alkyl combinations.

$$\alpha = r_{\text{TRMHx2}} + r_{\text{TTMP1}} + 2(r_{\text{TMOd}} + r_{\text{HMHxd}} + r_{\text{PMHpd}})$$
$$+ r_{\text{C}_{3}\text{H}_{6}} + 2r_{\text{DMBd}} + r_{\text{MB}2}$$

 $\beta = (r_{\rm C_3H_8} + r_{\rm CH_4})/\alpha$

The paraffin: alkene ratio is 0.90 ± 0.11 , indicating that no major product of the reaction was missed. The conversion ranges of DMB2 and AIP were 0.3-2.8% and 2.7-19.8%, respectively.

On the basis of the mechanism proposed, C_3H_8 , C_3H_6 and DMBa were expected to be major products of the reaction. 2,3,3,4-Tetramethylpentane (TMPa) was expected as the product of combination of iP[•] and 2,3-dimethylbut-2-yl radicals [DMB2[•] formed from the secondary decomposition of the combination product of iP[•] and μ_2 radicals^{8.9} (Scheme 1)]. Another possible source of TMPa is the disproportionation and H-abstraction of TMP2[•] formed in the addition of iP[•] to DMB2.

 \dagger Supplementary data SUP 56888 (3pp.) deposited with the British Library. Details available from the Editorial Office.

[a	ble	1	Products	of tl	he react	ion of	DM	IB2	and	AIP

		concentration (mol%) ^a	
compound	method of identification	1	2
CH₄	GC	0.98	0.83
C_2H_6	GC	0.10	
C_3H_8	GC	47.86	52.82
C_3H_6	GC	4.82	3.24
$i - \tilde{C}_4 \tilde{H}_{10}$	GC	0.15	
i-C ₄ H ₈	GC	0.42	
2-methylbut-2-ene (MB2)	GC	1.16	1.43
2,3-dimethylbuta-1,3-diene (DMBd)	GC	0.77	1.24
2,3-dimethylbutane (DMBa)	GC, MS	7.58	4.77
2,3-dimethylbut-1-ene (DMB1)	GC, MS	< 0.1	< 0.1
acetone isopropylidenehydrazone ^b	MS ^c	1.09	0.61
acetone isopropylhydrazone ^b	MS ^c		
2,3,3, 4-tetramethylpent-1-ene (TTMP1)	MS	6.33	5.10
2,3,5-trimethylhex-2-ene (TRMHx2)	MS	18.30	14.30
2,3,3,5,6-pentamethylhepta-1,5-diene (PMHpd)	MS		
2,3,3,4,4,5-hexamethylhexa-1,5-diene (HMHxd)	MS	3.50	5.20
2,3,6, 7-tetramethylocta-2,6-diene (TMOd)	MS	6.83	10.10

^a 1, $[DMB2]_0 = 1.50 \times 10^{-3} \text{ mol } dm^{-3}$, $[AIP]_0 = 3.05 \times 10^{-4} \text{ mol } dm^{-3}$, T = 520 K, t = 900 s. 2, $[DMB2]_0 = 1.50 \times 10^{-3} \text{ mol } dm^{-3}$, $[AIP]_0 = 1.00 \times 10^{-4} \text{ mol } dm^{-3}$, T = 520 K, t = 1200 s. ^b The GC response factor is supposed to be 6.0. ^c Ref. 13.

Table 2 Initial rate of formation of the products in the reaction of DMB2 and AIP ($[DMB2]_0 = 1.90 \times 10^{-3} \text{ mol dm}^{-3}$, $[AIP]_0 = 3.05 \times 10^{-4} \text{ mol dm}^{-3})^a$

	$r/10^{-9}$ mol dm ⁻³ s ⁻¹							
	540 K	535 K	530 K	525 K	520 K	500 K	495 K	490 K
CH4	3.36	2.92	1.71	1.02	0.615	0.150	0.0794	
C_3H_8	180	140	95.3	64.9	40.6	8.24	5.04	3.14
C_3H_6	25.6	16.8	10.2	7.16	2.64	0.395	0.195	0.110
MB2	(6.85)	4.40	2.88	2.41		0.280	0.124	
DMBd	4.59	2.88	1.51	0.703	0.386	0.0662	0.0245	
DMBa	43.2	33.9	18.9	10.6	4.60	0.594	0.342	
TRMHx2	80.3	63.7	41.7	24.8	15.2	2.30	1.207	0.652
TTMP1	27.6	21.9	14.4	8.47	5.26	0.828	0.448	0.243
PMHPd HMHxd	12.1	10.5	7.72	5.74	3.75	0.975	0.620	0.418
TMOd	23.5	19.6	15.0	11.0	7.12	1.89	1.17	0.815
t _{av.} /s	210	220	300	480	750	1950	3150	3300

" The abbreviations are given in Table 1.

(1) $(CH_3)_2CHN = NCH(CH_3)_2 \longrightarrow 2 CH_3\dot{C}HCH_3 + N_2$ H abstraction $\longrightarrow CH_3CH_2CH_3 + (CH_3)_2C = C(CH_3)\dot{C}H_2$ (2) $CH_3\dot{C}HCH_3 + (CH_3)_2C = C(CH_3)_2$ (TMA') (3) $CH_3\dot{C}HCH_3 + (CH_3)_2CHN = NCH(CH_3)_2 \longrightarrow CH_3CH_2CH_3 + (CH_3)_2CHN = N\dot{C}(CH_3)_2$ \longrightarrow CH₄ + (CH₃)₂C=C(CH₃)ĊH₂ (4) $\dot{C}H_3 + (CH_3)_2C = C(CH_3)_2$ (5) $\dot{C}H_3 + (CH_3)_2CHN = NCH(CH_3)_2$ \longrightarrow CH₄ + (CH₃)₂CHN=NĊ(CH₃)₂ (6) $(CH_3)_2 CH\dot{C}(CH_3)_2 + (CH_3)_2 C = C(CH_3)_2 \longrightarrow (CH_3)_2 CHCH(CH_3)_2 + (CH_3)_2 C = C(CH_3)\dot{C}H_2$ bond scission (7) $(CH_3)_2C(CH_3)_2CN = NCH(CH_3)_2 \longrightarrow (CH_3)_2CH\dot{C}(CH_3)_2 + CH_3\dot{C}HCH_3 + N_2$ $(iP\mu_2)$ (DMB2') (8) (CH₃)₂CHĊ(CH₃)₂ \longrightarrow $\dot{C}H_3 + (CH_3)_2C = CHCH_3$ combination \longrightarrow (CH₃)₂CHCH(CH₃)₂ (9) 2 CH₃ĊHCH₃ (10) $CH_3\dot{C}HCH_3 + (CH_3)_2C = C(CH_3)\dot{C}H_2 \longrightarrow (CH_3)_2C = C(CH_3)CH_2CH(CH_3)_2$ \rightarrow CH₂=C(CH₃)C(CH₃)₂CH(CH₃)₂ (11) \longrightarrow (CH₃)₂C=C(CH₃)CH₂CH₂C(CH₃)=C(CH₃)₂ (12) 2 $(CH_3)_2 C = C(CH_3)\dot{C}H_2$ \longrightarrow (CH₃)₂C=C(CH₃)CH₂C(CH₃)₂C(CH₃)=CH₂ (13) \longrightarrow CH₂=C(CH₃)C(CH₃)₂C(CH₃)₂C(CH₃)=CH₂ (14)(15) $CH_3\dot{C}HCH_3 + (CH_3)_2CHN = N\dot{C}(CH_3)_2 \longrightarrow (CH_3)_2CHN = NC(CH_3)_2C(CH_3)_2$ (16) $CH_3\dot{C}HCH_3 + \dot{C}H_3$ \longrightarrow (CH₂)₂CH $\longrightarrow C_2H_6$ (17) $\dot{C}H_3 + \dot{C}H_3$ disproportionation \longrightarrow CH₂=CHCH₃ + CH₃CH₂CH₃ (18) 2 CH₃CHCH₃ \longrightarrow (CH₃)₂CHC(CH₃)=CH₂ + CH₃CH₂CH₃ (19) $CH_3\dot{C}HCH_3 + (CH_3)_2CH\dot{C}(CH_3)_2$ \longrightarrow (CH₃)₂C=C(CH₃)CH₂ + CH₃CH₂CH₃ (20) \longrightarrow (CH₃)₂CHCH(CH₃)₂ + CH₂=CHCH₃ (21)(22) $CH_3\dot{C}HCH_3 + \dot{C}H_3$ \rightarrow CH₂=CHCH₃ + CH₄ (23) $CH_3\dot{C}HCH_3 + (CH_3)_2C = C(CH_3)\dot{C}H_2 \longrightarrow CH_2 = C(CH_3)C(CH_3) = CH_2 + CH_3CH_2CH_3$ (24) $CH_3\dot{C}HCH_3 + (CH_3)_2CHN = N\dot{C}(CH_3)_2 \longrightarrow product + CH_3CH_2CH_3$ \longrightarrow product + CH₃CH₂CH₃ (25)(26) \rightarrow product + CH₃CH=CH₂ ------ products (27) 2 (CH₃)₂CHN=NĊ(CH₃)₂ isomerization

 $(28) CH_2 = C(CH_3)C(CH_3)_2C(CH_3)_2C(CH_3) = CH_2 \longrightarrow (CH_3)_2C = C(CH_3)CH_2CH_2C(CH_3) = C(CH_3)_2C(CH_3)_2C(CH_3) = C(CH_3)_2C(CH_3)_2C(CH_3) = C(CH_3)_2C(CH_3)$

Scheme 1 Suggested mechanism for the reaction of DMB2 and AIP

TMPa was found in the thermal decomposition of pure AIP¹⁶ as the combination product of iP' and DMB2'. It is present at *ca.* 5% of the DMBa concentration in the temperature range 500–540 K.¹⁶ In the reaction of isobutene and AIP at 495–535 K, no TMPa was observed.¹⁶ The retention index of TMPa is similar to that of TTMP1. The concentration ratio TTMP1 : TRMHx2 (see later) is constant and independent of the temperature, within experimental error, which supports the assumptions that the formation of TMPa and the stationary concentration of TMP2' are negligible.

Acetone isopropylhydrazone (AIH) and acetone isopropylidenehydrazone (AIPH) are formed as ca. 0.6-1% of the total reaction products in the tautomerization of AIP and disproportionation of the μ_2 radical.

The initial concentrations of the reactants were corrected¹⁷ to allow for the small, but non-negligible, consumption of the

reactants given by eqn. (1) and (2):

$$[DMB2] = [DMB2]_0(1 - r_{DMB2} t_{av}/2)$$
(1)

$$[AIP] = [AIP]_0(1 - r_{AIP} t_{av}/2)$$
(2)

where t_{av} is the average reaction time considered in the calculation of the initial rates of formation and r_{DMB2} and r_{AIP} are the combined rates of formation of the products formed from DMB2 and AIP:

$$-r_{AIP} = (r_{C_{3}H_{8}} + r_{C_{3}H_{6}} + r_{CH_{4}} + 2r_{DMBa} + r_{TRMHx2} + r_{TTMP1} + r_{MB2})/2$$
(3)
$$-r_{DMB2} = r_{DMBd} + r_{TRMHx2} + r_{TTMP1}$$

$$+ 2(r_{\rm TMOd} + r_{\rm HMHxd} + r_{\rm PMHpd})$$
(4)

Thus, the 'initial' rates estimated are averages obtained in the early stages of the reaction. The temperature dependences of the rate constant ratios were calculated by the method of weighted non-linear least squares. The errors are the standard deviations. The units of $k_i/k_j^{1/2}$, k_0 and E are dm^{3/2} mol^{-1/2} s^{-1/2}, s⁻¹ and kJ mol⁻¹, respectively, and $\theta = RT \ln 10$.

Mechanism of the Reaction

In the reaction mechanism (Scheme 1) all the kinetically significant elementary reactions yielding the products identified are included: *i.e.* the formation of the predominant radicals (iP' and TMA'), and the possible H-abstraction, combination and disproportionation reactions of these radicals. iP' addition to DMB2 to yield the TMP2' radical was not taken into account (see later). In the self-combinations of allyl radicals, methyl-substituted hexa-1,5-dienes are formed. Cope rearrangements of these products¹⁸ result in changes in the composition of the products even in the early stages of the reaction.

Concentrations of the Predominant Radicals

Determination of the kinetic parameters was based on the assumption that the concentration of radicals is quasistationary in almost the whole conversion range of the initial rate determination. The quasi-stationary concentrations of the radicals were eliminated from the rate expressions *via* the initial rates of formation of combination products:

$$[iP'] = (r_{\rm DMBa}/k_9)^{1/2}$$
(5)

$$[TMA^*] = \left\{ \frac{(r_{TMOd} + r_{HMHxd} + r_{PMHpd})}{(k_{12} + k_{13} + k_{14})} \right\}^{1/2}$$
(6)

Cope Rearrangement and the Cross-combination Rule

The Cope rearrangements of pure HMHxd and TMOd have not yet been studied. The experiments of Doering *et al.*¹⁸ with dimethyl-substituted hexa-1,5-dienes revealed no Cope rearrangement at 389–440 K. Thermochemical calculations indicate that the equilibrium position of the reaction of HMHxd and TMOd is shifted to the right at these temperatures ($K = [TMOd]/[HMHxd] \approx 10^7$). Estimation of the thermochemical data by the MM2 method¹⁹ predicts a 39.6 kJ mol⁻¹ difference in the strain energies of these compounds. Thus, the major driving force of this reaction is the intramolecular strain in HMHxd.

The role of the Cope rearrangement was studied at 389– 540 K. The ratio $r_{TMOd}/(r_{PMHpd} + r_{HMHxd})$ vs. T is depicted in Fig. 1. (No separation of PMHpd and HMHxd could be attained with the analytical method applied.) The values at 389-440 K are from the reaction of DMB2 and DTBP.²⁰

It can be concluded from Fig. 1 that the Cope rearrangement is fast enough to convert practically all the HMHxd formed into TMOd at temperatures of 490 K and higher.

In order to establish whether the observed distribution of dienes is really a consequence of the Cope reaction, experiments were carried out in a di-*tert*-butyl peroxide + DMB2 reaction system at 540 K. The ratio $r_{\rm TMOd}/(r_{\rm HMHxd} + r_{\rm PMHpd})$ was found to be 1.92 ± 0.05 ([DMB2]₀ = 1.90×10^{-3} mol dm⁻³, [DTBP]₀ = 3.0×10^{-4} mol dm⁻³, $t_{\rm R} = 300$ and 600 s, respectively) which shows that the ratio is independent of the initiator used, and supports our conclusion concerning the importance of the Cope rearrangement at these high temperatures.



Fig. 1 Effect of temperature on the ratios of initial rates for dienes: (•) DMB2 + DTBP, 389 < T/K < 440; (○) DMB2 + AIP, 490 < T/K < 540

We conclude from the experimental data shown in Fig. 1 that product consumption is kinetically controlled at the lowest temperatures and, consequently, an extrapolation to zero reaction time yields the rate constant ratio

$$\frac{r_{\text{TMOd}}}{r_{\text{HMHxd}} + r_{\text{PMHpd}}} = \frac{k_{12} [\text{TMA}^{*}]^{2}}{k_{13} [\text{TMA}^{*}]^{2} + k_{14} [\text{TMA}^{*}]^{2}}$$
$$= \frac{k_{12}}{k_{13} + k_{14}} = 0.98 \pm 0.07$$

(calculated from the 389–398 K data). On the other hand, at temperatures over 490 K practically all of the HMHxd is converted into TMOd. Under such conditions, the assumed rate of accumulation of TMOd can be given as the sum of r_{12} and r_{13} . When all the points given in Fig. 1 were fitted with the function y = aT/(1 + bT), where a/b is the limiting value of y (*i.e.* assuming that practically all of the HMHxd is rearranged into TMOd), a value

$$\frac{r_{12} + r_{13}}{r_{14}} = \frac{k_{12} [\text{TMA}^{-}]^2 + k_{13} [\text{TMA}^{-}]^2}{k_{14} [\text{TMA}^{-}]^2}$$
$$= \frac{k_{12} + k_{13}}{k_{14}} = 1.95$$

was obtained. From this datum and from $(k_{12} + k_{13})/k_{14} = 0.98$, the following rate constant ratios were calculated:

$$k_{12}/k_{14} = 1.46; \quad k_{13}/k_{14} = 0.49$$
 (7)

The initial rates of TMA[•] combination products not influenced by the Cope rearrangements were estimated using eqn. (7):

$$r_{12} = 0.49(r_{\text{TMOd}} + r_{\text{HMHxd}} + r_{\text{PMHpd}})$$

$$r_{13} = 0.17(r_{\text{TMOd}} + r_{\text{HMHxd}} + r_{\text{PMHpd}})$$

$$r_{14} = 0.34(r_{\text{TMOd}} + r_{\text{HMHxd}} + r_{\text{PMHpd}})$$

From the data given in eqn. (7), the cross-combination ratio, ϕ ,

$$\phi(\text{TMA}^{\prime}, \text{TMA}^{\prime}) = \frac{k_{14}}{(k_{12}k_{13})^{1/2}} = \frac{r_{14}}{(r_{12}r_{13})^{1/2}} = 1.2$$
 (8)

was obtained.

iP' and TMA' combine to form TRMHx2 and TTMP1. ϕ obtained for the terminal (t) combination is

$$\phi(iP', TMA')_{t} = \frac{k_{10}}{(k_{9}k_{12})^{1/2}}$$

= $\frac{r_{TRMHx2}}{(r_{12}r_{DMBa})^{1/2}} = 2.4 \pm 0.3$ (9)

and that for the non-terminal (n) combination is

$$\phi(iP^{*}, TMA^{*})_{n} = \frac{k_{11}}{(k_{9}k_{13})^{1/2}}$$

= $\frac{r_{TTMP1}}{(r_{13}r_{DMBa})^{1/2}} = 1.6 \pm 0.2$ (10)

 ϕ for the overall combination of iP[•] and TMA[•] at t and n positions is

$$\phi(iP^{*}, TMA^{*})_{t+n} = \frac{k_{10} + k_{11}}{\{k_{9}(k_{12} + k_{13} + k_{14})\}^{1/2}}$$
$$= \frac{r_{TRMHx2} + r_{TTMP1}}{\{(r_{HMHxd} + r_{TMOd} + r_{PMHPd})r_{DMBa}\}^{1/2}} = 2.4 \pm 0.3 \quad (11)$$

The ratio of the t and n cross-combination products of the iP' and TMA' radicals is temperature independent at 490-540 K:

$$k_{10}/k_{11} = r_{\text{TRMHx2}}/r_{\text{TTMP1}} = 2.8 \pm 0.1$$
 (12)

which supports the conclusion that the concentration of even the first adduct radical is negligible. Baulch *et al.*¹¹ obtained a considerably higher value $(k_{10}/k_{11} = 8 \pm 2 \text{ at } 297 \pm 1 \text{ K})$.

The values obtained for ϕ (TMA⁺, TMA⁺), ϕ (iP⁺, TMA⁺), and ϕ (iP⁺, TMA⁺)_n are at variance with ϕ predicted by hardsphere collision theory for radicals with the same masses and collision diameters.²¹ Studies on other radicals resulted in values close to 2 for both the cross-reaction ratio and ϕ .^{21–25} Recently, Anastasi and Arthur²⁵ published a datum for the combination of methyl and *tert*-butyl radicals ($\phi = 1.3$). Garland and Bayes²⁶ also observed differences from ϕ for some small alkyl radicals [*e.g.* ϕ (CH⁺₃, C₃H⁺₅) = 1.6].

Disproportionation-Combination Ratios of the Isopropyl and 1,1,2-Trimethylallyl Radicals

The products of the self-disproportionation reaction of iP' are C_3H_8 and C_3H_6 . DMBa is formed in the combination (see later). The disproportionation-combination ratio was determined to be between 0.5 and 0.8.1-6.8 In the decomposition of pure AIP, $r_{C_3H_6}/r_{DMBa}$ was found to depend on the temperature and initial concentration. Acs et al.⁸ suggested a primary H-atom abstraction by iP' from AIP, and decomposition of the μ_1 radical formed. On the basis of their experimental results, Görgényi and Seres¹⁶ suggested that the rate constant for the primary H-atom abstraction is overestimated. We repeated the experiments of Szirovicza and Márta²⁷ with $[AIP]_0 = 2.47 \times 10^{-4} \text{ mol } dm^{-3}$ and $[neo-C_5H_{12}]_0 = 2.47 \times 10^{-3} \text{ mol } dm^{-3}$ at 544 K to establish the relative amounts of isobutene and DMBa. Supposing that the primary H atoms in neopentane and AIP are of equal reactivity and that the neopentyl radical decomposes almost quantitatively into CH₃ and isobutene, the rate constant for the primary H-atom abstraction from the methyl groups of AIP⁸ by iP' is ca. $\frac{1}{50}$ of the value suggested.⁸

The ratio of the product of iP^* disproportionation (C_3H_6) and self-combination (DMBa) was found to vary within experimental error. Eqn. (13), below, was obtained to describe the disproportionation-combination ratio of iP^* . By averaging the data,

$$\frac{r_{C_3H_6}}{r_{DMBa}} = \Delta(iP^*, iP^*) = 0.58 \pm 0.06 \tag{13}$$

This value is in good agreement with some literature data $[\Delta(iP^*, iP^*) = 0.50, {}^10.54, {}^20.49 - 0.52, {}^50.51, {}^80.59^{16}]$, although other data are considerably higher $(1.05, {}^{28}0.80^{29})$.

In the disproportionation of iP[•] and TMA[•] [reaction (23)], DMBd and C_3H_8 are formed, while the t and n combinations yield TRMHx2 and TTMP1, respectively. The disproportionation-combination rate constant ratio is

$$\frac{k_{23}[iP^*][TMA^*]}{(k_{10} + k_{11})[iP^*][TMA^*]} = \frac{r_{DMBd}}{r_{TRMHx2} + r_{TTMP1}}$$
$$= \Delta(iP^*, TMA^*) = 0.03 \pm 0.01 \quad (14)$$

This value is in reasonable agreement with the results of Montague,¹⁰ Baulch *et al.*¹¹ and Klein *et al.*¹² who obtained Δ (**R**[•], TMA[•]) \approx 0.01 at 293 \pm 1 K. Δ (**R**[•], TMA[•]) was stated to be significantly larger than Δ (TMA[•], **R**[•]),¹⁰⁻¹² which is valid in our experience.

Unimolecular Decomposition Rate Constant of Azoisopropane

The Arrhenius parameters of the rate constant of the thermal decomposition of AIP were determined as a means of calibration of the method. These quantities are known in the literature.¹⁻⁶ Determination of k_1 is rendered difficult by the occurrence of a chain component whose contribution to the formation of the measured products has not been elucidated so far. It was hoped that the present system would allow a more precise determination of k_1 , since the contribution of the chain processes was substantially decreased by the abundance of the alkene over AIP.

The decomposition rate constant of AIP was estimated by summation of the rates of formation of products incorporating iP':

$$r_{1} = (r_{C_{3}H_{6}} + r_{C_{3}H_{8}} + 2r_{DMBa} + r_{TRMHx2} + r_{TTMP1})/2$$

$$r_{1} = k_{1}[AIP]$$
(15)

The rate constant ratios are listed in Table 3. The temperature dependence of the rate constant is given by

$$\log(k_1/s^{-1}) = (16.36 + 0.49) - (201.5 \pm 5.4) \text{ kJ mol}^{-1}/\theta$$

where the error limit of A was increased from the random errors value by a factor of 2, with a corresponding increase in the error of E. The rate constant is $1.31 \times 10^{-4} \text{ s}^{-1}$ at 520 K, which is in the lower region of the data published earlier $(1.17 \times 10^{-4}, ^{5} 1.90 \times 10^{-4} \text{ s}^{-1}, ^{5} 2.77 \times 10^{-4} \text{ s}^{-1}, ^{8} 2.96 \times 10^{-4} \text{ s}^{-1}$ indicating a substantial oppression of the chain component in the decomposition of AIP.

H Abstraction from 2,3-Dimethylbut-2-ene by the Isopropyl Radical

In the H abstraction of the iP' radical from DMB2, Pa and the TMA' radical are formed [Scheme 1, reaction (2)]. The rate of H abstraction determined from C_3H_8 formation, is

$$r_{2} = k_{2}[iP^{*}][DMB2]$$

= $r_{C,H_{2}} - r_{C,H_{2}} - r_{DMBd} - k_{3}[iP^{*}][AIP]$ (16)

 $= r_{C_3H_8} - r_{C_3H_6} - r_{DMBd} - k_3[iP^*][AIP]$ (16) where corrections were made for the C₃H₈ formed in disproportionation and in H abstraction from AIP.

$$k_{3}[iP^{*}][AIP] = \frac{k_{3}}{k_{9}^{1/2}} r_{DMBa}^{1/2}[AIP]$$
 (17)

For $k_3/k_9^{1/2}$ the value of Görgényi and Seres¹⁶ was used $[\log(k_3/k_9^{1/2}) = 4.10 - 43.6 \text{ kJ mol}^{-1}/\theta].$

 Table 3
 Rate constants and rate constant ratios calculated by eqn. (15) and (16)

$[DMB2]_0/10^{-3} \text{ mol dm}^{-3}$	$[AIP]_0/10^{-4} \text{ mol dm}^{-3}$	T/K	$k_1/10^{-6} \text{ s}^{-1}$	$(k_2/k_9^{1/2})/dm^{3/2} \text{ mol}^{-1/2} \text{ s}^{-1/2}$
		(495	12.7	0.0925
	3.00	500	21.7	0.118
		520	125	0.220
1.90		\$ 525	218	0.214
		530	344	0.234
		535	541	0.251
		540	705	0.280
		500	21.0	0.0979
		510	43.7	0.129
1.90	1.00	{ 520	129	0.202
		525	201	0.231
		530	320	0.231
		(495	13.4	0.0866
		500	20.3	0.104
		510	55.5	0.153
1.50	3.00	520	130	0.202
		525	216	0.215
		(530	352	0.235
		(500	19.9	0.112
		510	48.0	0.167
		520	131	0.184
1.50	1.00	{ 525	223	0.234
		530	360	0.267
		535	442	0.242
		L 540	678	0.285
1.10	3.00	§ 510	54.0	0.153
	1.00	ر 510	54.4	0.150

The calculated rate constant ratios are listed in Table 3. The following Arrhenius parameters were obtained:

$$\log[(k_2/k_9^{1/2})/dm^{3/2} \text{ mol}^{-1/2} \text{ s}^{-1/2}] = (4.99 \pm 0.49)$$

 $-(57.0 \pm 5.4) \text{ kJ mol}^{-1}/\theta$

where the error limit of A was increased from the random errors value by a factor of 2, with a corresponding increase in the error of E. By using the rate constant of iP[•] radical self-combination^{28,30} (log $k_9 = 9.6$), the Arrhenius expression is

$$\log k_2 = (9.79 \pm 0.49) - (57.0 \pm 5.4) \text{ kJ mol}^{-1}/6$$

There are no published data with which to compare this result; however, the rate constants of H abstraction by iP' from C_3H_6 and isobutene have been determined: $\log(k_{C_3H_6}/k_9^{1/2}) = (3.4 \pm 0.3) - (45.2 \pm 3.3) \text{ kJ mol}^{-1}/\theta,^{13}$ and $\log(k_{i-C_4H_6}/k_9^{1/2}) = (4.39 \pm 0.17) - (55.3 \pm 1.0) \text{ kJ mol}^{-1}/\theta,^{31}$ Even if we consider the unusually large reaction path degeneracy of 12, the pre-exponential factor obtained here is higher than expected and so is the activation energy. For the H abstraction of the CH₃ radical from DMB2, a similar high pre-exponential factor and activation energy were obtained.²⁰ The rate constant ratios are more in line with expectation: 0.072 for C_3H_6 ,¹³ 0.069 for isobutene³¹ and 0.19 for DMB2 at 520 K. The initial rates of product formation are summarized in the tables of the supplementary material (see footnote on p. 2446).

This work has been carried out with the financial support of the Hungarian Ministry of Education (749/86) and the Hungarian Research Foundation (OTKA 394/88).

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Paper 1/06506H; Received 30th December, 1991