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Reactions of Unsymmetrically Substituted Allyl Radicals with Methyl Radicals

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Abstract

The $Hg(6^3P_1)$ photosensitized decompositions of 3-methyl-1-butene, 2-methyl-2-butene, 3,3-dimethyl-1-butene, and 2,3-dimethyl-1-butene have been used to generate 1-methylallyl, 1,2-dimethylallyl, 1,1-dimethylallyl, and 1,1,2-trimethylallyl radicals in the gas phase at 24 ± 1°C. From a study of the relative yields of the CH_3 combination products, the relative reactivities of the reaction centers in each of these unsymmetrically substituted ambident radicals have been determined. The more substituted centers are found to be the less reactive, and this is ascribed primarily to greater steric interaction at these centers during reaction. Measurement of the ratio of *trans*- to *cis*-2-pentene formed from the 1-methylallyl radical, combined with published values for this ratio at higher temperatures, enabled the differences in entropy and heat of formation of the *trans*- and *cis*-forms of this radical to be calculated as 0.62 ± 0.85 J mol^{-1}K^{-1} and -0.63 ± 0.25 kJ mol^{-1}, respectively, at 298K. Approximate values of the disproportionation/combination ratios for reaction of CH_3 with 1,1-dimethylallyl and 1-methylallyl have been estimated and used to compute rate constants for the recombinations of *tert*-butyl and isopropyl radicals that are in agreement with recently published data.

1. Introduction

Studies of the geometric isomerization of substituted allylic radicals have been carried out for several years [1,2], and recently preliminary measurements of the rates of some of these interconversions have been reported [3,4]. In addition to isomerization, unsymmetrically substituted allylic radicals can react by combination with other radicals yielding, as a result of their ambident nature, more than one product. As yet the literature contains little quantitative information on the relative reactivities of the reactive centers in such radicals undergoing combination despite the presence of these processes in many olefin pyrolyses and other complex reaction systems, e.g., those of $CH_2(^3B_1)$ with olefins. During the course of a study of the $Hg(6^3P_1)$-photosensitized rearrangements of various olefins in the gas phase, information concerning both the relative isomer stabilities and the combination with methyl radicals of some substituted allylic radicals has been obtained and is now reported.

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2. Experimental

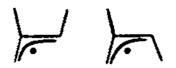
Reactant gases were handled on a conventional all-Pyrex, grease-free vacuum line constructed with Pyrex needle valves (J. Young Ltd., Teflon sealing O-rings). A Hanovia spiral low-pressure mercury lamp (Type 752/62) was used to photolyze the samples which were contained in a 35-ml cylindrical cell equipped with a 5-cm-diameter fused silica window and closed by a Springham greaseless stopcock (Viton A diaphragm). Mercury vapor was provided by a clean mercury droplet. The olefins used in this study, 3-methyl-1-butene (Matheson Co., Inc.), 2-methyl-2-butene (Phillips Petroleum Co.), 3,3-dimethyl-1-butene (Aldrich Chemical Co.), and 2,3-dimethyl-1-butene (Chemical Samples Co.), showed $<0.2\%$ total impurities when analyzed by gas chromatography. As none of the products of interest was present among these trace impurities, the olefins were used without further purification, except for thorough degassing in vacuo. The percentage conversion of the olefins was always $<0.5\%$.

Reaction mixtures were analyzed either on a 100-m wall-coated polypropylene glycol capillary column at 0°C or a 45 ft. × $\frac{1}{8}$ in. silicone oil and Poropak combination column at 75°C. The two Perkin-Elmer gas chromatographs used (452 and F11) were each fitted with a flame ionization detector. Products were identified by comparing their relative retention times with those of authentic samples, and their relative yields were estimated either by planimetry or by ball-and-disc integration of the chart recorder output. Isomeric compounds were assumed to give equal detector response signals per aliquot.

3. Results and Discussion

Of the eleven polymethyl-substituted allyl radicals, six are unsymmetric, and of these, four have been investigated in the present study. They are the 1-methylallyl or butenyl (I), 1,2-dimethylallyl (II), 1,1-dimethylallyl (III), and 1,1,2-trimethylallyl (IV) radicals:


I


II


III


IV

A. *1-Methylallyl radical (I)*

The $Hg(6^3P_1)$-photosensitized decomposition of 3-methyl-1-butene (3MB) was studied at 24°C in the pressure range 12–764 Torr.[1] Rupture of the weak C_3—C_4 bond following energy transfer produces I as shown in eq. (1):

$$(1) \qquad Hg(6^3P_1) + 3MB \rightarrow Hg(6^1S_0) + CH_3 + I$$

Vibrationally excited 1,2-dimethyl-1,3-trimethylene biradicals are also formed in

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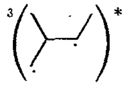
[1] 1 Torr = 133.3 N m^{-2}.

this reaction system [5]; and, in competition with collisional deactivation and cyclization, they may decompose by methyl loss [6], also yielding I as in eq. (2):

(2)



$$\rightarrow \text{I} + \text{CH}_3$$

Combination of the radical fragments formed in reactions (1) and (2) produces 2-pentene (2P) and 3MB according to the following reaction scheme:

$$\textit{cis}\text{-I} \rightleftharpoons \textit{trans}\text{-I} \tag{3}$$

$$\textit{cis}\text{-I} + \text{CH}_3 \rightarrow \text{3MB} \tag{4}$$

$$\textit{cis}\text{-I} + \text{CH}_3 \rightarrow \textit{cis}\text{-2P} \tag{5}$$

$$\textit{trans}\text{-I} + \text{CH}_3 \rightarrow \text{3MB} \tag{6}$$

$$\textit{trans}\text{-I} + \text{CH}_3 \rightarrow \textit{trans}\text{-2P} \tag{7}$$

No geometric isomerization of the chemically activated 2P molecules formed in reactions (5) and (7) can occur as essentially all are collisionally deactivated in the pressure range of these experiments.

The formation of 2P by a pathway involving a 1,2-methyl shift in the 1,2-dimethyl-1,3-trimethylene biradical can be ruled out by the results of experiments in which oxygen (6.0–37.0%) was added to the reaction mixture. The yields of all monoradical products, including 2P, fell to zero in these experiments in contrast to those of products produced by unimolecular reactions of the triplet olefin and biradical, which were only partially reduced [7].

If the assumption is made that the rate of radical isomerization, reaction (3), is sufficiently rapid to maintain *cis*-I and *trans*-I in their stationary state equilibrium concentrations, then a kinetic analysis of the reaction scheme shows that the experimentally observed ratio R_I of the yields of *trans*- and *cis*-2P to that of 3MB is given by

$$\frac{[\textit{trans}\text{-2P} + \textit{cis}\text{-2P}]}{[\text{3MB}]} = R_\text{I} = \frac{(\alpha_c\beta + \alpha_t K_\text{I})}{(\beta + K_\text{I})} \tag{8}$$

and the ratio Q_I of the yield of *trans*-2P to *cis*-2P is given by

$$\frac{[\textit{trans}\text{-2P}]}{[\textit{cis}\text{-2P}]} = Q_\text{I} = \frac{\alpha_t K_\text{I}}{\alpha_c \beta} \tag{9}$$

where $\alpha_c = k_5/k_4$, $\alpha_t = k_7/k_6$, $\beta = k_4/k_6$, and $K_\text{I} = k_3/k_{-3}$. α_c and α_t reflect the relative reactivity of the less substituted to more substituted reactive center in *cis*-I and *trans*-I, respectively. These experiments do not allow R_I to be evaluated. However, data from the Hg(6^3P_1)-photosensitized decompositions of 1-butene [8] and 3,4-dimethyl-Δ^1-pyrazoline [9] at room temperature enable values of 2.25 ± 0.2 and 2.0 ± 0.2 to be estimated, while at higher temperatures (126.0–

163.0°C) it has been suggested [10] that R_{I} is as high as 3.0 ± 0.2. If $\alpha_t = \alpha_c = \alpha_{\mathrm{I}}$, then R_{I} is equal to α_{I}.

A value of 1.39 ± 0.02 was obtained for Q_{I} from an average of 25 separate experimental determinations at room temperature (24 ± 1°C). No variation in this ratio with pressure could be detected. A few experiments were also carried out under conditions such that the photolysis light intensity incident on the cell was reduced by an order of magnitude. Again, the measured value of Q_{I} was the same. Higher total pressure and lower light intensity both reduce the rates of reactions (5) and (7). Therefore, as Q_{I} remained constant, it is concluded that *trans*-I and *cis*-I are maintained in their equilibrium ratio in every experimental run. Thus, unless *trans*-I and *cis*-I are fortuitously produced by reactions (1) and (2) in exactly this ratio, the rate of radical isomerization must be sufficiently rapid so as to compete effectively with reactions (5) and (7) under these conditions.[2] The 1-butene [8] and pyrazoline [9] decomposition data enable Q_{I} values of 1.3 ± 0.1 and 1.4 ± 0.05 to be calculated, in agreement with the value found here. Yokoyama and Brinton have obtained data [11] from which Q_{I} may be calculated [10] at higher temperatures.

A plot of $\log_{10} Q_{\mathrm{I}}$ against the reciprocal of absolute temperature is shown in Figure 1. The slope of this plot is $(\Delta E - \Delta H)/2.303R$, where ΔE is the activation energy of reaction (5) less that of reaction (7). Despite the large uncertainties in Q_{I} at high temperature, $(\Delta E - \Delta H)$ may be estimated from the plot to be 0.63 ± 0.25 kJ mol^{-1}. This is a *maximum* value, as it is reduced by placing greater weight on the point at 410.1K. Therefore, if ΔE is zero and $\alpha_t = \alpha_c\beta$, i.e., $Q_{\mathrm{I}} = K_{\mathrm{I}}$, then at 25°C, $\Delta H^0 = -0.63 \pm 0.25$ kJ mol^{-1}, $\Delta G^0 = -0.814 \pm 0.035$ kJ mol^{-1}, and $\Delta S^0 = 0.62 \pm 0.85$ J mol^{-1}K^{-1}. Small positive values of ΔE will clearly decrease the difference in heats of formation of *trans*-I and *cis*-I but will not affect the value of ΔG^0 as long as the assumption $k_5 = k_7$ holds. Thus, it would appear that, while the *trans*-radical has the lower heat of formation, ΔH^0 and ΔS^0 are numerically smaller than the corresponding values for the isomeric olefins of analogous structure, *trans*- and *cis*-2-butene [12]. Equivalent ΔH^0 values for the radical and olefin pairs would require that ΔE should be approximately -3.5 kJ mol^{-1}. This seems unlikely, however, as it implies that the 2-pentene of lower heat of formation is produced by the higher energy pathway.

The difference in ΔH^0 and ΔS^0 for the two isomeric pairs are largely determined by gauche interactions in the *cis*-isomers. The data therefore imply that this interaction is less in *cis*-I than in *cis*-2-butene. This conclusion can be rationalized by considering the structures of the two molecules. Thus, when a primary hydrogen atom is removed from *cis*-2-butene, the change in hybridization

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[2] Calculations of the relative rates of radical isomerization vs. combination with CH_3 based on the Arrhenius parameters of reaction (3) (D. M. Golden, *Int. J. Chem. Kinet.*, **1**, 127 (1969)), the stationary state methyl radical concentration computed from the known rate of formation of ethane, and estimated rate constants for reactions (5) and (7) (vide infra) substantiate this conclusion.

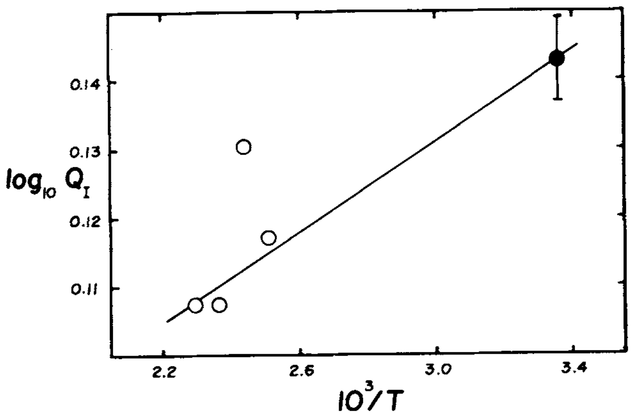


Figure 1. Variation of $\log_{10}Q_I$ with temperature: (●) this work; (○) data from reference [10].

at C_1 and the lengthening of the C_2—C_3 bond coupled with a shortening of the C_1—C_2 bond cause the average distance between the hydrogen atoms on C_1 and those on C_4 to increase, thereby decreasing their steric interaction and the hindrance to internal rotation of the methyl group.

Estimates of K_I have been obtained at different temperatures in other systems. Preliminary data for the addition of HI to 1,3-butadiene [13] at 90°C and for the dimerization [3] of I at 125.7°C give $K_I = 1.2 \pm 0.2$ and 1.45, respectively. Within experimental error, both of these values are compatible with that of Q_I obtained here.

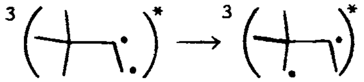
B. *1,2-Dimethylallyl radical (II)*

A *cis-* and *trans-*mixture of radical II was generated at room temperature in the presence of methyl radicals by three methods. The $Hg(6^3P_1)$-sensitized decomposition of 2,3-dimethyl-1-butene (23DMB), in the pressure range 20–57 Torr, gives II, as in reaction (10), by a reaction analogous to (1):

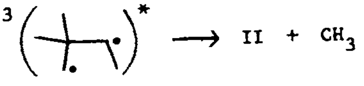
$$Hg(6^3P_1) + 23DMB \rightarrow Hg(6^1S_0) + CH_3 + II \tag{10}$$

II was also produced by the mercury-photosensitized decompositions of 3,3-dimethyl-1-butene (33DMB) and 2-methyl-2-butene (2MB) in the pressure ranges 20–100 Torr and 9–27 Torr, respectively. In the former system, rearrangement to the vibrationally excited 1,2,2-trimethyl-1,3-trimethylene biradical occurs, reaction (11). Subsequent decomposition of this biradical gives II, as shown in reaction (12):

(11)



(12)



2MB gives radical II by the well-characterized [14] hydrogen atom loss reaction,

(13) $Hg(6^3P_1) + 2MB \rightarrow Hg(6^1S_0) + H + II$

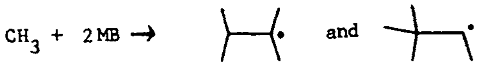
The mechanism by which CH_3 radicals are produced in this latter system is not certain. It is probable, however, that they arise by decomposition of excited 3MB and 2-methyl-1-butene formed by 1,3-hydrogen shifts in excited triplet 2MB.

Combination of CH_3 with II proceeds by a sequence of reactions analogous to those involving I, reactions (3)–(7). The values for the ratio of *trans*- to *cis*-3-methyl-2-pentene, Q_{II}, obtained in the 23DMB, 33DMB, and 2MB systems from 5, 6, and 4 experimental determinations, respectively, were 1.29 ± 0.02, 1.27 ± 0.02, and 1.26 ± 0.03. Although no confirmation was obtained, it is probable that rotational equilibration of the isomeric forms of II was complete prior to reaction with CH_3, as in the case of I. Thus, if $Q_{II} = K_{II} = 1.28 \pm 0.02$, it is the form of the 1,2-dimethylallyl radical in which the methyl groups are cis to one another that has the greater stability at 25°C.

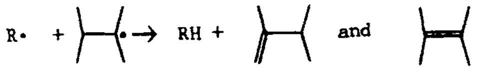
R_{II}, the product ratio of 3-methyl-2-pentene to 23DMB, was measured in both the 33DMB and 2MB experimental systems. Values of 1.81 ± 0.04 and 1.83 ± 0.04 were obtained. If the reactivity of the unsubstituted reaction center in *cis*-II relative to that in *trans*-II equals β_{II}, then $R_{II} = \alpha_{II}$.

23DMB can also be produced from 2MB by disproportionation, as in reaction (15), of the 2,3-dimethylbut-2-yl radical formed by methyl radical addition to the parent olefin, reaction (14):

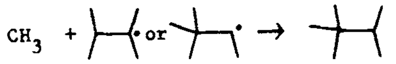
(14)



(15)



(16)



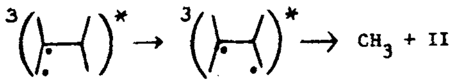
However, as the yields of 2,3-dimethyl-2-butene and 2,2,3-trimethylbutane, produced in reaction (16), were both small in these runs (<1% and <3%, respectively, of the total yield of 23DMB), it seems unlikely that the contribution of reaction (15) to the 23DMB yield would be greater than 1%.

C. *1,1-Dimethylallyl radical (III)*

Reactions (17) and (18) generate the 1,1-dimethylallyl radical in the 3MB and 23DMB systems, respectively:

(17) $Hg(6^3P_1) + 3MB \rightarrow Hg(6^1S_0) + H + III$

(18)



The ratio ($R_{III} = \alpha_{III}$) of 2-methyl-2-pentene (2MP) to 3,3-dimethyl-1-butene formed by combination of III with CH_3 in the 23DMB experiments was 5.7 ± 0.2 and was pressure independent within the limited pressure range of the study. In the 3MB system, however, R_{III} increased by a factor of $\sim 15\%$ as the total pressure increased from 12 to 764 Torr. A concomitant increase in the relative yields of 2-methylpentane and 2,3-dimethylpentane was observed, as was the appearance of 4-methyl-2-pentene. These latter products can be accounted for by a mechanism postulating addition of CH_3 to 3MB, followed by disproportionation, combination with CH_3, and abstraction of H by the resulting 2-methylpent-3-yl radical. This radical can also disproportionate to 2MP. In order to reduce the observed 2MP yield to that arising solely by radical recombination, the contribution from disproportionation, estimated by arbitrarily equating it to the yield of 4-methyl-2-pentene, was subtracted. Applying this correction virtually eliminated the pressure dependence of R_{III}, giving a value of 6.1 ± 0.6.

D. *1,1,2-Trimethylallyl radical (IV)*

Radical IV, produced in the mercury-sensitized 23DMB decomposition, as shown in reaction (19),

$$\text{(19)} \qquad \text{Hg}(6^3P_1) + \text{23DMB} \rightarrow \text{Hg}(6^1S_0) + \text{H} + \text{IV}$$

combines with CH_3 to give 2,3-dimethyl-2-pentene (23DMP) and 2,3,3-trimethyl-1-butene (233TMB), in a ratio α_{IV}. The experimental ratio, R_{IV}, of 23DMP to 233TMB was 3.25 ± 0.5. 23DMP can also be formed, as can 3,4-dimethyl-2-pentene (34DMP), by disproportionation of the 2,3-dimethylpent-3-yl radical present in this system. However, as only trace quantities of 34DMP were found, the disproportionation yield of 23DMP was presumed to be small and has therefore been neglected.

E. *Summary of radical combination data*

A summary of the product ratios obtained is shown in Table I. The data clearly demonstrates that the reaction center with greater methyl substitution is the less reactive in regard to combination with CH_3. A similar trend in reactivity has been observed in studies of the dimerization of both the 1-methylallyl [3] and 1,1-dimethylallyl radicals [15,16]. 1,1-Dichloroallyl radicals also display a degree of selectivity on self-recombination [17], and nonequivalent relative reactivities for the reaction centers of other ambident delocalized radicals engaged in atom abstraction have been reported [18,19]. The factors determining the product distributions in abstraction and combination reactions of this type have been discussed [15,18]. For combination, where the energy barrier is very low or even nonexistent, the effects of steric interaction and relative spin density at the radical reaction centers are dominant. However, as the ESR spectra of methyl-substituted allyl radicals show that the relative spin densities do not deviate

TABLE I. Product ratios[a] from substituted allyl radical combination with methyl radicals at 24 ± 1°C.

Ratio	System[a]				
	23DMB	33DMB	2MB	3MB	Other
Q_{I}	—	—	—	1.39 ± 0.02	1.3 ± 0.1^{b} 1.4 ± 0.05^{c}
Q_{II}	1.29 ± 0.02	1.27 ± 0.02	1.26 ± 0.03	—	—
R_{I}	—	—	—	—	2.25 ± 0.2^{b} 2.0 ± 0.2^{c}
R_{II}	—	1.81 ± 0.04	1.83 ± 0.04	—	—
α_{III}	5.7 ± 0.2	—	—	6.1 ± 0.6	—
R_{IV}	3.25 ± 0.5	—	—	—	—

[a] See text for explanation of symbols.
[b] Reference [8].
[c] Reference [9].

significantly from unity [2], the latter effect must be unimportant. It is therefore the greater steric inhibition toward combination at the more substituted center which ensures that the observed α values are greater than 1.0. Such an effect is seen to exert its maximum influence in the case of the 1,1-dimethylallyl radical.

Combination of any one substituted allylic radical with radicals other than methyl would be expected to give different values for α. Thus, analysis of the data of Engel et al. [14,15] leads to lower values for α_{III} of 1.88 and 1.80 for combination of III with the two localized forms of III, 3-methyl-1-buten-3-yl and 3-methyl-2-buten-1-yl, respectively. The decrease in α_{III} results from the larger size and more bulky nature of each of the latter radicals reducing the combination reaction selectivity by making the magnitudes of the steric interactions for each pathway less disparate. Radical IV displays a similar decrease in selectivity as compared to III, for combination with CH_3. In this case it is methyl substitution at C_2 that results in α_{IV} being less than α_{III}. By analogy, it might be expected that R_{I} would be greater than R_{II} as the difference in substitution pattern of radicals I and II is identical to that of radicals III and IV. In contrast to this prediction, however, R_{I} and R_{II} are found to be equal within the limits of experimental error. It therefore seems clear that a quantitative evaluation of the individual steric interactions within the reacting radical pair that combine to determine the overall relative reactivities of the reaction centers is at present unattainable.

F. *Radical disproportionation*

Small yields of products arising from the disproportionation of allylic radicals were also observed. Disproportionation/combination ratios could not be determined accurately, however, owing to the complex nature of the reactions and the presence of several different radicals in each system. Nevertheless, approximate values for $\Delta(CH_3,III)$ and $\Delta(CH_3,I)$ of 0.1 and 0.02, respectively, were obtained from the yields of isoprene versus 33DMB and 1,3-butadiene versus 3MB (given by $2P/R_1$) in the 3MB experiments. These estimates neglect any contribution to product yields from the disproportionation of allylic radicals with radicals other than CH_3. Such contributions are, however, likely to be small as reactions of CH_3 and I predominate in this system [7].

The $\Delta(CH_3,III)$ value can be used to enable a crude value of the rate constant for combination of *tert*-butyl radicals to be calculated from the reported rate constant for allyl radical recombination [20]. Three assumptions are necessary for this calculation. They are (i) the rate constant for 2MP formation from CH_3 and III is one half that for the combination of CH_3 with allyl; (ii) the disproportionation rate constants per hydrogen atom available for transfer for the reactions of CH_3 with both III and *tert*-butyl are equal; and (iii) the root-mean-square rule [21] can be successfully applied to the cross-combinations of CH_3 with both allyl and *tert*-butyl. It may then be shown that the rate constant k_c for the dimerization of *tert*-butyl radicals is given by

$$k_c = \frac{9[\Delta(CH_3,III)]^2 k_a}{16[\Delta(CH_3,t\text{-Bu})]^2(\alpha_{III})^2} \tag{20}$$

where $k_a = 10^{12.92}$ cm^3 mol^{-1} s^{-1}, the rate constant for allyl radical combination at 298K [20], and $\Delta(CH_3,t\text{-Bu})$ is the disproportionation/combination ration for methyl plus *tert*-butyl. Substituting $\alpha_{III} = 5.7$ and using $\Delta(CH_3,t\text{-Bu}) = 0.81$ [22],

$$k_c = 10^{9.34} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1} \text{ at 298K}$$

Using a proposed [23] lower value for $\Delta(CH_3,t\text{-Bu})$ of 0.656 and assuming that $\Delta(CH_3,III)$ could be as high as 0.2 results in an increase in k_c by a factor of 6. Thus, even allowing for large errors in the disproportionation/combination ratios, the calculated value of k_c remains at least three orders of magnitude lower than the accepted rate constant for methyl radical recombination [24] ($10^{13.386}$ cm^3 mol^{-1} s^{-1} at 298K). The present estimate, although somewhat speculative, therefore provides support for the recently redetermined recombination rate constant for *tert*-butyl radicals of $10^{8.6\pm1.2}$ cm^3 mol^{-1} s^{-1}, measured at 462K [25].

A similar calculation based on analogous assumptions to those postulated can be performed to compute k_c', the rate constant for recombination of isopropyl radicals, from $\Delta(CH_3,I)$. k_c' is given by

$$k_c' = \frac{[\Delta(CH_3,I)]^2 k_a}{[\Delta(CH_3,i\text{-Pr})]^2(\alpha_I)^2} \tag{21}$$

where $\Delta(CH_3,i\text{-Pr})$ is the disproportionation/combination ratio for CH_3 plus isopropyl. Several literature values for $\Delta(CH_3,i\text{-Pr})$ are available [26], of which the more recent value of 0.163 is used here [27]. Numerical substitution in eq. (21) leads to $k_c' = 10^{10.5}$ cm^3 mol^{-1} s^{-1}, which may be compared with Hiatt and Benson's experimentally determined value of $10^{11.6\pm1.1}$ cm^3 mol^{-1} s^1 obtained at 415K [28].

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