Clearly there are still problems in this area despite the "simplicity" of the electronic spectra of copper(II). Some 10% of the 40 or more complexes which have been investigated in these studies are badly behaved and are therefore signalling structural or electronic abnormalities which are at present unclear. Complexes of 1,3-diaminopropane are all badly behaved; compare, for example, Tables I and II. Possibly this reflects the greater conformational freedom of the six-membered rings in these complexes. Once these abnormalities have been explained and understood, and some enthalpy data become available for compounds with a substituent other than water, then the correlations discussed here lay a secure foundation for the evaluation of bond strengths from solid state electronic data.

Acknowledgments. We are indebted to the National Research Council (Canada) for financial support and to Professor Paoletti of the University of Florence for samples of certain tetraamine complexes and for permission to quote some of his data prior to publication.

The Kinetics of the Positional Isomerization of 2,3-Dimethyl-2-butene. The Heat of Formation of the 2,3-Dimethylbutenyl Radical and the Effect of Methyl Substituents on the Allyl Radical Stabilization Energy[1a]

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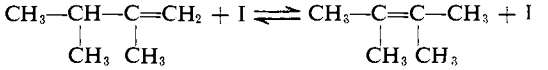
Abstract: The iodine atom catalyzed isomerization, I + 2,3-dimethyl-1-butene $\rightleftharpoons$ 2,3-dimethyl-2-butene + I (k_1, k_2), has been studied from 410 to 530°K. The reaction was found to be surface catalyzed in glass reaction vessels but homogeneous from 477 to 530°K in Teflon coated glass reaction vessels. The rate constant k_1 in this range was given by: $\log (k_1/\text{l. mol}^{-1}\ \text{sec}^{-1}) = (7.36 \pm 0.12) - (6.28 \pm 0.28)/\theta$. From these data the enthalpy of formation of the 2,3-dimethylbutenyl radical (DM-BR) was calculated as: $\Delta H_f°(\text{DM-BR, g, 298}) = 9.6 \pm 1$ kcal mol^{-1}. The bond dissociation energies of the primary C–H bond in 2,3-dimethyl-2-butene is $DH°(C_p\text{–H}) = 78.0 \pm 1$, and the tertiary C–H bond in 2,3-dimethyl-1-butene is $DH°(C_t\text{–H}) = 76.3 \pm 1$ kcal mol^{-1}. Consequently, the stabilization energy of the dimethylbutenyl radical is 16.7 to 18.5 kcal mol^{-1} depending on the localized model used. When this is compared with the stabilization energies of the allyl and butenyl radicals one is led to the conclusion that the methyl group increases the stabilization energy of the allyl radical by approximately 3 kcal mol^{-1} per group.

Approximately 10 yr ago Benson and Bose[2] proposed a free radical mechanism for the iodine catalyzed positional isomerization of olefins. This was closely followed by a study of the positional isomerization of 2-butene by Egger, Golden, and Benson[3] from which the stabilization energy[4] of the butenyl radical (methallyl) was determined as 12.4 ± 1.4 kcal mol^{-1}. Subsequently, Golden, Rodgers, and Benson[5,6] showed that the stabilization energy of the allyl radical was 9.5 ± 1.4 kcal mol^{-1}, a value recently confirmed by equilibrium studies.[7] In addition to establishing the low value for the allyl radical stabilization energy (*i.e.*, 10–12 rather than 16 to 25 kcal mol^{-1}),[7] these data also indicated that methyl substituents on the allyl radical may increase the stabilization energy. To further pursue this point we have undertaken this study of the kinetics of the iodine atom catalyzed positional isomerization of 2,3-dimethyl-1-butene (eq 1) from which the



$$\underset{\substack{|\\ CH_3}}{} CH_3\text{—}\underset{\substack{|\\ CH_3}}{CH}\text{—}\underset{\substack{|\\ CH_3}}{C}\text{=}CH_2 + I \rightleftharpoons CH_3\text{—}\underset{\substack{|\\ CH_3}}{C}\text{=}\underset{\substack{|\\ CH_3}}{C}\text{—}CH_3 + I \qquad (1)$$

(DM-1B) (DM-2B)

stabilization energy of the 2,3-dimethylbutenyl radical may be deduced. As this is an allyl radical with three methyl substituents, any such effect should become obvious. The equilibrium constant for reaction 1, needed for the kinetic analysis, has been reported earlier.[8]

Experimental Section

The apparatus has been described in detail previously.[8] Briefly, it consists of a reaction vessel connected to a "hot" box. The temperature of the hot box is maintained at 80–100° so that iodine may be handled and measured up to 40 Torr. The pressure measurements are made in the hot box with a Pace-Wiancko pres-

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[1] (a) This research was supported by the Robert A. Welch foundation. (b) Robert A. Welch predoctoral fellow, 1969–1970.

[2] S. W. Benson, A. N. Bose, and P. Nangia, *J. Amer. Chem. Soc.*, **85**, 1388 (1963).

[3] K. W. Egger, D. M. Golden, and S. W. Benson, *J. Amer. Chem. Soc.*, **86**, 5420 (1964).

[4] For a discussion of the relative merits of stabilization as opposed to resonance energy see: A. S. Rodgers, M. C. R. Wu, and L. Kuitu, *J. Phys. Chem.*, **76**, 918 (1972).

[5] D. M. Golden, A. S. Rodgers, and S. W. Benson, *J. Amer. Chem. Soc.*, **88**, 3196 (1966).

[6] D. M. Golden and S. W. Benson, *Chem. Rev.*, **69**, 125 (1969).

[7] D. M. Golden, N. Gac, and S. W. Benson, *J. Amer. Chem. Soc.*, **91**, 2136 (1969).

[8] A. S. Rodgers and M. C. R. Wu, *J. Chem. Thermodyn.*, **3**, 591 (1971).

sure transducer used as a null device, the pressures being read either on an oil manometer ($P < 60$ Torr) or on a Hg manometer ($P > 60$ Torr). Connections are made through the hot box to a product analysis train and thence to a glc and to a conventional vacuum system in which purified reactants are stored. The product analysis train and traps were painted black to limit photolytic isomerization of the reactant mixture during handling. Blank runs have indicated less than 0.25% reaction. The temperature of the reaction vessel (400–500°K) was maintained to ±0.25°K in a wire wound aluminum oven. The tubing connecting the reaction vessel to the isolating stopcock in the hot box was wrapped with heating tape and kept at 120–150°. The volume of this tubing, the dead space for this system, was approximately 2 cm^3, generally less than 1% of the total reaction volume.

The reaction procedure is described as follows. Iodine was first admitted to the reaction vessel at the desired temperature and the pressure measured. Then the chosen 2,3-dimethylbutene was added and the pressure determined once again. Then, after an appropriate time interval, a sample of the reaction mixture, approximately equal to twice the dead space volume, was taken and discarded; then another sample was taken by rapidly expanding the reaction mixture into a 70-cm^3 trap filled with Ascarite and chilled in an ice bath. This froze the reaction mixture and removed the iodine and hydrogen iodide. The time interval, Δt, was recorded. The gases were then expanded into a second trap for gas–liquid chromatographic analysis. This was accomplished at 25° using a Model 90-P Varian Aerograph gas chromatograph and a 0.6 × 152 cm column packed with 20% dimethylsulfolane on 60–80 Chromosorb W. At a helium flow rate of 44 cm^3 min^{-1}, the air peak showed at 1 min after injection. The C_6 hydrocarbons showed the following retention times measured from the air peak (in minutes): 2,3-dimethylbutane, 1.6; 2,3-dimethyl-1-butene, 2.8; 2,3-dimethyl-2-butene, 6.3; and 2,3-dimethyl-1,3-butadiene, 9.5. The accuracy of the glc analysis was ±2% and was determined from standard mixtures of the 2,3-dimethylbutenes analyzed under simulated experimental conditions. The results of these measurements gave

$$\frac{\text{peak area of DM-2B}}{\text{peak area of DM-1B}} = (1.05 \pm 0.01)\frac{p(\text{DM-2B})}{p(\text{DM-1B})}$$

Peak areas were determined from the formula

$$\text{area} = \text{peak height} \times \text{width at half height}$$

The rate constant was calculated by eq 2 if DM-1B were the starting material and by eq 3 if DM-2B were the starting material.

$$k_1 = -[\Delta t(1 + K^{-1})]^{-1} \ln \left[1 - (1 + K^{-1})\frac{P_2}{P_1 + P_2}\right] \qquad (2)$$

$$k_1 = -K[\Delta t(1 + K)]^{-1} \ln \left[1 - (1 + K)\frac{p_1}{p_2 + p_1}\right] \qquad (3)$$

$$K = k_1/k_2 \qquad (4)$$

In eq 2 and 3, p_1 and p_2 are the partial pressures of DM-1B and DM-2B, respectively, at the end of the time interval, Δt. It is assumed in these equations that no other reaction is taking place so that $p_1 + p_2 = p_0$. The side reactions yielding 2,3-dimethylbutadiene and 2,3-dimethylbutane reported previously[8] were generally less than 1% for p_0 of these experiments. The equilibrium constant, K, was evaluated according to eq 5.[8]

$$\ln K = -0.427 + 544/T - \ln (T/486) \qquad (5)$$

The reaction was found to be surface sensitive so that several reaction vessels were used. Reaction vessel R-1 was coated with silicone oil as described by Egger and Benson;[9] its volume was approximately 500 cm^3. Reaction vessel R-2 was packed with Raushing rings and then coated with silicone oil as above; its volume was approximately 200 cm^3 and its surface to volume ratio was 11 times larger than R-1. Reaction vessel R-3 was coated with a Teflon slurry obtained from the E. I. du Pont de Nemours Co. and then heated, with ventilation, up to 350° (just above the glass transition) for 10 min. This was very similar to a coating process used by Rodgers[10] and found effective in fluorination. The vessel was repeatedly coated by this procedure until no further reduction in the rate of reaction was experienced; approximately five coats of Teflon were required. Its volume was approximately 500 cm^3. The effect of surface upon this reaction is illustrated by the results given in Table I. The reaction is highly surface sensitive in silicone-treated glass reactors (R-1). As will be seen subsequently, there appears to be a surface component at very low temperatures in the Teflon coated vessel; however, evidence shall be presented that shows that this residual surface reaction is negligible for temperatures greater than 477°K.

Table I. Apparent Rate Constant for the Positional Isomerization of 2,3-Dimethyl-1-butene for Various Reaction Vessels

Rxn vessel	Temp, °K	I_2/Torr	DM-1B, Torr	$k_1/10^4$ l. mol^{-1} sec^{-1}
R-2 (packed)[a]	444	7.9	71.6	69.9
R-1	444	8.2	44.2	6.7
R-3 (Teflon)	444	4.9	38.1	2.47
R-2 (packed)[a]	519	8.3	63.7	10.6
R-1	516	2.7	67.3	5.1
R-3 (Teflon)	515	4.7	42.5	4.75

[a] Surface area/volume area is 11 times that of R-1 or R-3.

Results

The results obtained for the rate constant k_1, calculated by eq 2 or 3, are summarized in Table II, and a plot of log k_1 *vs.* 1000/T is shown in Figure 1. It is evident, from a consideration of these data, that at least two different processes are taking place and, from

Table II. Rate Constants for the Positional Isomerization of 2,3-Dimethyl-1-butene

T, °K	Time, sec	p_{I_2}, Torr	p_{olefin}, Torr	% rxn	$k_1/10^4$ l. mol^{-1} sec^{-1}
529.15	727	4.14	DMB-2;34.9	84	6.03
529.8	625	4.54	DMB-1;34.5	80	5.71
530.60	431	5.29	DMB-2;32.5	71	5.85
529.65	482	5.63	DMB-1;38.5	75	5.76
514.9	380	4.46	DMB-2;37.0	40	4.92
514.9	760	4.67	DMB-1;42.5	63	4.75
504.15	466	4.49	DMB-2;43.0	31	4.33
504.15	428	4.59	DMB-1;47.0	30	4.67
504.15	1624	4.60	DMB-1;39.0	73	4.29
504.15	942	4.62	DMB-1;43.0	53	4.24
491.4	1092	4.42	DMB-2;37.5	38	3.73
491.4	1660	4.53	DMB-1;50.5	50	3.50
477.4	1731	4.52	DMB-2;35.0	30	3.04
477.65	2000	4.30	DMB-1;33.7	33	3.01
477.65	1501	5.31	DMB-2;33.5	29	3.03
477.4	1300	6.91	DMB-1;42.0	29	3.07
477.4	5631	10.69	DMB-2;31.0	83	3.00
460.4	3073	4.58	DMB-2;34.9	23	2.49
460.4	6837	4.65	DMB-1;38.8	45	2.52
446.9	6207	4.88	DMB-2;32.1	26	2.46
446.9	6620	4.52	DMB-1;35.0	27	2.51
446.9	18192	4.53	DMB-2;39.5	59	2.60
444.65	3865	4.68	DMB-2;40.3	15	2.45
444.65	21295	5.03	DMB-1;35.0	64	2.68
444.65	7340	4.89	DMB-1;38.1	28	2.47
444.65	14778	4.92	DMB-2;35.1	48	2.48
430.15	16055	4.55	DMB-1;37.9	44	4.15
430.15	7957	4.80	DMB-2;34.2	21	3.39
428.5	12995	3.82	DMB-2;28.3	34	4.41
428.5	5863	11.06	DMB-2;13.6	35	5.98
429.9	8590	11.41	DMB-1;42.4	46	5.29
411.9	16850	4.83	DMB-1;36.7	27	5.31

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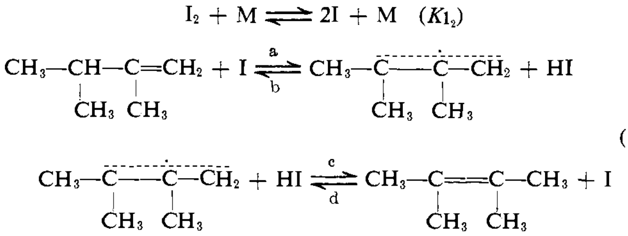
(9) K. W. Egger and S. W. Benson, *J. Amer. Chem. Soc.*, **87**, 3314 (1965).

(10) A. S. Rodgers, *J. Phys. Chem.*, **67**, 2799 (1963).

the positive slope at lower temperatures in Figure 1, a low-temperature process is taking place that does not depend upon the iodine atom concentration. This is also indicated by the results at 429°K (Table II), in which k_1 is seen to increase with increasing iodine partial pressure. It is suggested that this low-temperature process is a heterogeneous reaction taking place on sites that have not been deactivated by the coating process or on sites that have been exposed due to fissures in the Teflon coat (the surface of the Teflon is visibly "mud caked"). Due to the negative temperature coefficient, one would expect this heterogeneous contribution to k_1 to become less important at higher temperatures. Indeed, at 477°K and above, the experimental values of k_1 are independent of the partial pressure of the olefin, iodine, and extent of reaction; and microscopic reversibility holds rigorously. This portion of the data is in excellent agreement with the expected homogeneous, free radical mechanism, namely[2,3]



$$\mathrm{I_2 + M \rightleftharpoons 2I + M} \quad (K_{\mathrm{I_2}})$$

$$\mathrm{CH_3{-}}\underset{\mathrm{CH_3}}{\mathrm{CH}}\mathrm{{-}}\underset{\mathrm{CH_3}}{\mathrm{C}}\mathrm{{=}CH_2 + I} \underset{b}{\overset{a}{\rightleftharpoons}} \mathrm{CH_3{-}}\underset{\mathrm{CH_3}}{\mathrm{C}}\mathrm{{-}{-}{-}}\underset{\mathrm{CH_3}}{\mathrm{C}}\mathrm{{-}{-}CH_2 + HI}$$

$$\mathrm{CH_3{-}}\underset{\mathrm{CH_3}}{\mathrm{C}}\mathrm{{-}{-}{-}}\underset{\mathrm{CH_3}}{\mathrm{C}}\mathrm{{-}{-}CH_2 + HI} \underset{d}{\overset{c}{\rightleftharpoons}} \mathrm{CH_3{-}}\underset{\mathrm{CH_3}}{\mathrm{C}}\mathrm{{=}{=}}\underset{\mathrm{CH_3}}{\mathrm{C}}\mathrm{{-}CH_3 + I}$$

(I)

At steady state, the rate of isomerization of DM-1B is given by

$$\text{rate} = \frac{k_c}{k_b + k_c} k_a[\text{DM-1B}][\text{I}] \qquad (6)$$

consequently

$$k_1 = k_a k_c/(k_b + k_c) \qquad (7)$$

A least-squares analysis of the results for k_1 from 477 to 530°K yields

$$\log (k_1/\text{l. mol}^{-1}\ \text{sec}^{-1}) = (7.36 \pm 0.12) - (6.28 \pm 0.28)/\theta \qquad (8)$$

from microscopic reversibility, one obtains

$$k_2 = k_d k_b/(k_c + k_b) \qquad (9)$$

$$\log (k_2/\text{l. mol}^{-1}\ \text{sec}^{-1}) = (7.97 \pm 0.12) - (8.30 \pm 0.28)/\theta \qquad (10)$$

The errors are twice the standard deviations, and $\theta = 2.303RT$ in kcal mol^{-1}.

Discussion

Golden and Benson have summarized the data on the activation energies of the radical abstractions of hydrogen from HI and have found that they fall in the range 1 ± 1 kcal mol^{-1}. It is of particular interest here that the activation energy for the allyl radical has been found to be 1 ± 1 kcal mol^{-1} also.[7] Consequently, one can reasonably expect $E_b = E_c = 1 \pm 1$ kcal mol^{-1} and, therefore, $E_a = E_1$ and $E_d = E_2$. The heats of reactions a and d can then be calculated from eq 8 and 10.

$$\Delta H_r°(\text{a,g,500°K}) = E_a - E_b = 6.28 - 1 = 5.3 \pm 1 \text{ kcal mol}^{-1}$$

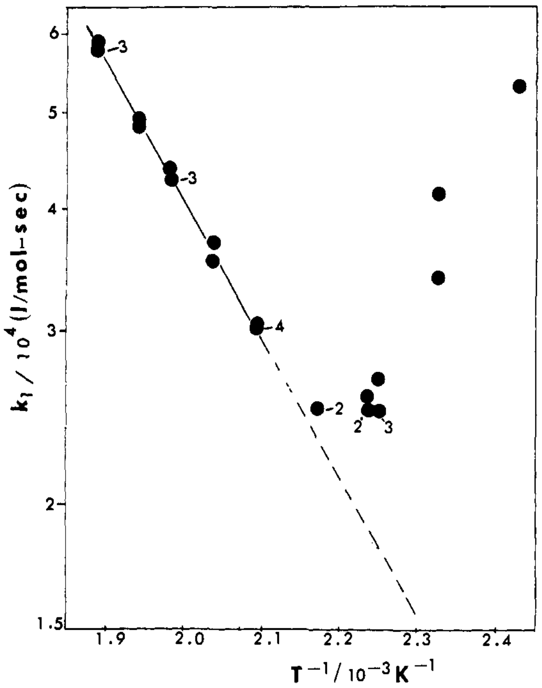


Figure 1. Arrhenius plot for the specific rate constant for the reaction 2,3-dimethyl-1-butene + I → 2,3-dimethyl-2-butene + I (k_1). (Numbers indicate overlapping points.)

$$\Delta H_r°(\text{d,g,500°K}) = E_d - E_c = 8.33 - 1 = 7.3 \pm 1 \text{ kcal mol}^{-1}$$

If one assumes that the heat capacity of the 2,3-dimethylbutenyl radical (DM-BR) is given approximately by eq 11, then, by group additivity,[11] the mean differ-

$$C_p°(\text{DM-BR,g,}T) = 0.5[C_p°(\text{DM-1B,g,}T) + C_p°(\text{DM-2B,g,}T)] \qquad (11)$$

ences in heat capacity for reactions a and d from 300 to 500°K are estimated as: $\langle \Delta C_p° \rangle_a = 1.1 \pm 1$ and $\langle \Delta C_p° \rangle_d = 3.0 \pm 1$ cal mol^{-1} K^{-1}. Thus, the heats of reaction at 298°K are

$$\Delta H_r°(\text{a,g,298}) = 5.0 \pm 1 \text{ kcal mol}^{-1}$$

$$\Delta H_r°(\text{d,g,298}) = 6.7 \pm 1 \text{ kcal mol}^{-1}$$

The heat of formation of DM-BR may then be calculated from these data and the heats of formation of DM-1B and DM-2B selected by Rodgers and Wu.[8] Thus, $\Delta H_f°(\text{DM-BR,g,298}) = 9.6 \pm 1.1$ kcal mol^{-1} and the primary C–H bond dissociation energies in DM-2B and the tertiary C–H bond in DM-1B become

$$DH°_{298}(\text{DM-2B,C}_p\text{–H}) = 78.0 \pm 1.1 \text{ kcal mol}^{-1}$$

$$DH°_{298}(\text{DM-1B,C}_t\text{–H}) = 76.3 \pm 1.1 \text{ kcal mol}^{-1}$$

The stabilization energy, as defined by Benson,[12] has recently been shown to be the best measure of the delocalization energy in free radicals.[4] For the 2,3-dimethylbutenyl radical, this can be defined in two ways; one, eq 12, is based upon the primary C–H bond dissociation energy in DM-2B, and the other, eq 13, is based upon the tertiary C–H bond in DM-1B.

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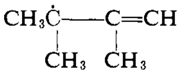
(11) S. W. Benson, *et al.*, *Chem. Rev.*, **69**, 279 (1969).

(12) S. W. Benson, *J. Chem. Educ.*, 42, 502 (1965).

$$SE^\circ_{298}(\text{DM-BR}) = DH^\circ_{298}(\text{Std},\text{C}_\text{p}\text{-H}) - DH^\circ_{298}(\text{DM-2B},\text{C}_\text{p}\text{-H}) + E_\text{c}(\text{DM-BR}) - E_\text{c}(\text{DM-2B}) \quad (12)$$

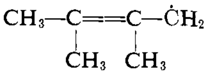
$$SE^\circ_{298}(\text{DM-BR}) = DH^\circ_{298}(\text{Std},\text{C}_\text{t}\text{-H}) - DH^\circ_{298}(\text{DM-1B},\text{C}_\text{t}\text{-H}) + E_\text{c}(\text{DM-BR}) - E_\text{c}(\text{DM-1B}) \quad (13)$$

In these equations, $DH^\circ_{298}(\text{Std,C-H})$ is the bond dissociation energy of the relevant C–H bond in the saturated or standard compound;[4] thus, $DH^\circ_{298}(\text{Std},\text{C}_\text{p}\text{-H}) = 98$ and $DH^\circ_{298}(\text{Std},\text{C}_\text{t}\text{-H}) = 92$ kcal/mol.[6] The configurational energy, E_c, has been determined by group additivity methods;[11] $E_\text{c}(\text{DM-2B}) = 3.0$ and $E_\text{c}(\text{DM-1B}) = 0.5$ kcal mol^{-1}. The value for E_c(DM-BR) has been estimated as $0.5E_\text{c}(\text{DM-2B}) = 1.5$ kcal mol^{-1}. When these values are substituted into eq 12 and 13, one obtains RHS(12) = 18.5 and RHS(13) = 16.7 kcal mol^{-1}. This divergence is not unexpected. The 2,3-dimethylbutenyl radical is a resonance hybrid of the valence bond structures II and III and the stabilization energy is a measure of the difference in energy between one such localized structure and the delocalized radical. Unless these structures (II and III) have the same energy, the calculated stabilization energy will depend upon which localized structure was used. Equation 12 is based upon the localized structure III while eq 13 is based upon II, and the difference in the calculated stabilization energies can be interpreted as the enthalpy of the hypothetical reaction e.



$\mathrm{CH_3\dot{C}(CH_3)\!-\!C(CH_3)\!=\!CH_2}$

II



$\mathrm{CH_3\!-\!C(CH_3)\!=\!C(CH_3)\!-\!\dot{C}H_2}$

III

$$\text{II} \xrightarrow{\text{e}} \text{III}$$

Thus, from eq 12 and 13, $\Delta H_\text{r}^\circ(\text{e},298) = 1.8$ kcal mol^{-1}. The enthalpy of reaction e can also be estimated by group additivity methods if one assumes that the groups $\cdot\text{C-(C}_\text{d}\text{)(H)}_2$ and $\cdot\text{C-(C}_\text{d}\text{)(C)}_2$, unique to structures II and III, are equal to their saturated counterparts $\cdot\text{C-(C)(H)}_2$ and $\cdot\text{C-(C)}_3$. This is consistent with the definition of stabilization energy.[4,12] Thus, the enthalpy of reaction e in this approximation is given by[11,13]

$$\Delta H_\text{r}^\circ(\text{e},298) = [(\text{C}_\text{d}\text{-(C)}_2] - [\text{C}_\text{d}\text{-(H)}_2] + [\cdot\text{C-(C)(H)}_2] - [\cdot\text{C-(C)}_3] = 2.2 \text{ kcal mol}^{-1} \quad (14)$$

This is in excellent agreement with the 1.8 kcal mol^{-1} obtained experimentally and indicates the degree of consistency in these two approaches.

The stabilization energy of the allyl and butenyl radicals is 9.5 ± 1.4[5,6] and 12.4 ± 1.4[3] kcal mol^{-1}, respectively, based upon the bond dissociation energy of the primary C–H bond in propene and *trans*-2-butene. The stabilization energy of the DM-BR is 18.5 kcal mol^{-1} based upon the bond dissociation energy of the primary C–H bond in DM-2B (eq 12). These results correspond to allyl radicals with 0, 1, and 3 methyl substituents and clearly indicate a substituent effect of approximately 3 kcal mol^{-1} per methyl group. This conclusion would remain essentially unchanged even if one used the lower value of 16.7 kcal mol^{-1} from eq 13.

In order to deduce the Arrhenius A factors for reactions a and d from eq 8 and 10, it is necessary to estimate a value for $k_\text{b}/(k_\text{b} + k_\text{c})$. Since $E_\text{b} = E_\text{c}$, this is equivalent to estimating A_b and A_c. One can calculate the A factors for the abstraction of hydrogen from HI for the ethyl, isopropyl, and tertiary butyl radicals from the corresponding data on these reactions[6] and estimated entropies for these free radicals.[13] When this is done one finds that they all fall within a factor of 3 of one another so that a reasonable approximation for $A_\text{b}/(A_\text{b} + A_\text{c})$, and therefore $k_\text{b}/(k_\text{b} + k_\text{c})$, is 0.5 ± 0.25. Thus, the Arrhenius A factors for reactions a and d are

$$\log (A_\text{a}/\text{l. mol}^{-1}\ \text{sec}^{-1}) \cong 7.7$$

$$\log (A_\text{d}/\text{l. mol}^{-1}\ \text{sec}^{-1}) \cong 8.3$$

These are low values for such atom abstraction reactions and must correspond to a very tight transition state.[14] They are, however, in line with other results on reactions of this type. A summary of the intrinsic A factors (*i.e.*, A factor divided by the number of equivalent hydrogens) for hydrogen abstraction by iodine from ethane, propene, *trans*-2-butene, and DM-2B are given in Table III. The decrease of 0.7 log unit from ethane to propene has been attributed to the loss of internal rotation in going from propene to the allylic transition state.[5] However, as can be seen from Table III, a further loss of 0.6 log unit is encountered in going from *trans*-2-butene to the methyl-substituted allylic transition state and a loss of 2.6 log units from DM-2B to a *tris*-methyl-substituted transition state, *i.e.*, a loss of about 0.8 log unit for each methyl substituent. There is, unfortunately, no obvious physical explanation for this observed trend. Certainly, it cannot be explained in terms of a loss of internal rotation of the methyl groups due to their interaction with the allylic π system, as this interaction is only 3 kcal mol^{-1} per methyl group and should be independent of orientation irrespective of its mechanism (*i.e.*, hyperconjugative or inductive). Neither can one explain the low A factor for DM-2B simply on the basis of tight transition state. A lower limit to the entropy of the transition state for reaction d can be estimated as at least equal to the entropy of 2,3-dimethyl-1-iodo-2-butene less 3.7 cal mol^{-1} K^{-1} for loss of internal rotation in the allylic structure. In the group additivity approximation, the

Table III. Arrhenius A Factors for the Abstraction Reaction: $\text{RH} + \text{I} \rightarrow \text{R}\cdot + \text{HI}$

RH	log (A/l. mol^{-1} sec^{-1}) − log N_H	Δ log A/N_H	Ref
CH_3CH_3	10.5		*a*
$\text{CH}_2\text{=CHCH}_3$	9.8	0.7	*a*
$\text{CH}_3\text{CH=CHCH}_3$	9.2	1.3	*b*
$\text{(CH}_3)_2\text{C=C(CH}_3)_2$	7.2	3.3	This work

[a] Reference 6. [b] Reference 3.

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entropy change from reactants to the transition state becomes

$$\Delta S^{\circ\ddagger} \cong [\mathrm{C{-}(C)(H)_3}] - [\mathrm{C{-}(C)(H)_2(I)}] - 3.7 + R \ln 12 - S^\circ(\mathrm{I,g,298}) \cong -30 \text{ cal mol}^{-1}\text{ K}^{-1} \quad [\langle \Delta C_p{}^\circ \rangle = 0] \quad (15)$$

This model should represent a very tight transition state[13] yet yields an A factor of $10^{9.0}$ l. mol^{-1} sec^{-1} at 500°K, a factor of 5 greater than observed. Thus, the trend toward lower A factors with sucessive methyl substitution, first indicated in the results for *trans*-2-butene and now confirmed in this work, must remain an anomaly until further work is done on related systems. It is interesting to note that, as is frequently the case, the decrease in the activation energy in these reactions is almost exactly compensated by this decrease in the A factors.

Finally, it is worthwhile to consider the dependence of our conclusions upon the estimation of E_b and E_c. Since, from thermochemistry[8]

$$DH^\circ_{298}(\mathrm{DM\text{-}2B,C_p{-}H}) - DH^\circ_{298}(\mathrm{DM\text{-}1B,C_t{-}H}) = 1.7 \text{ kcal mol}^{-1}$$

it would be very unlikely that $|E_b - E_c| > 2$ kcal mol^{-1} even if E_b and E_c should prove greater than the estimated 1 kcal mol^{-1}. As a result then, $k_b/(k_b + k_c)$ and $k_c/(k_b + k_c)$ will still be temperature independent and $E_a = E_1$ and $E_d = E_2$ as before. However, the bond dissociation energies would now be given by

$$DH^\circ_{298}(\mathrm{DM\text{-}2B,C_p{-}H}) = 78.0 - (E_c - 1.0) \text{ kcal mol}^{-1}$$

and

$$DH^\circ_{298}(\mathrm{DM\text{-}1B,C_t{-}H}) = 76.3 - (E_b - 1.0) \text{ kcal mol}^{-1}$$

They would become weaker!

Thus, while our quantitative results depend upon the estimation of E_b and E_c, the general conclusion that the allyl radical is stabilized by methyl substituents (and by about 3 kcal mol^{-1} per group) does not.

Kinetics of Competing Free Radical Reactions with Nitroaromatic Compounds

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Abstract: Rate constants for the competing reactions between alcohol donor free radicals and nitroaromatic compounds, and their relative efficiencies, have been measured by pulse radiolysis. The kinetics of formation of the nitroaromatic anion species are dependent upon the sum of the rate constants for both competing reactions and not upon the rate constant for radical oxidation alone. The rate constants for donor radical oxidation and adduct formation increase with increasing redox potential of the electron acceptor. Although α- and β-hydroxy radicals have similar reactivities, α-hydroxy radicals are oxidized preferentially whereas β-hydroxy radicals predominantly form adducts.

The high reactivity of free radicals with organic nitro compounds and other electron acceptors is well recognized. Electron-transfer oxidation by nitro compounds of $\cdot CO_2H$ or $\cdot CO_2^-$, α-hydroxy, and α-alkoxy radicals has been demonstrated by electron spin resonance studies.[1–4] Alkyl and β-hydroxy radicals and the radicals $\cdot OH$ and $\cdot NH_2$, on the other hand, react readily by addition to the electron acceptor.[5–7] The rates of alkyl radical adduct formation,[5,6] like those of α-hydroxy radical oxidation,[3,8] increase with increasing redox potential of the electron acceptor. We have studied the kinetics of these competing donor free radical reactions with nitroaromatic compounds by direct observation of the reactive species, using the technique of pulse radiolysis.[9] The extent of donor radical oxidation is obtained from the yield of the transient radical anion of the nitro compound, and the rate constants for radical oxidation and adduct formation are determined from the rates of build-up of the nitroaromatic radical anion for different concentrations of nitro compound, according to the kinetic analysis described. These data are particularly important in the study of chemical and biological radiosensitization.[8,10,11] Electron-affinic compounds,[11] particularly nitroaromatic and nitroheterocyclic compounds, are believed to radiosensitive at low concentrations by

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