sodium acetate (25 mg) and zinc dust (750 mg) for 4 hr and the filtered solution poured into sodium acetate solution (2 N). After 1 hr the latter solution was extracted with chloroform (2 × 50 cc) and the chloroform extracts washed with sodium bicarbonate solution and water. Evaporation of the solvent gave a brown gum which was dissolved in benzene (5 cc) and absorbed on a column of precipitated silica (12 × 4 cm, in benzene) and the yellow orange band eluted with further benzene (350 cc). Evaporation of the benzene gave a light orange solid which crystallised from acetic anhydride as an orange powder (15 mg) m.p. 245–250° (d). (Found: C, 69·8, H, 4·4; Calc. for $C_{21}H_{20}O_{6}$: C, 69·4, H, 4·1%). Light absorption in $CHCl_3$: max at 396, 421, and 450 mμ; log ε 4·15, 4·40, and 4·51 respectively; min at 404 and 432 mμ; log ε 4·13 and 4·23.

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Electron transference in the attack of atoms or radicals upon carbon-hydrogen bonds

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Prof. J. Kenner has recently discussed a number of reactions wherein carbon-hydrogen bonds are broken and alkyl free radicals thereby generated.[1] His interpretation is that this process should always be formulated as involving two or more steps with electron transference being the dominant and initial process.

$$R-H \cdot X\cdot \longrightarrow \overset{+}{R\cdot H}\ X: \longrightarrow R\cdot \cdot H-X$$

Although I agree in principle to the importance of electron transference in the reactions of atoms and radicals having a high electron affinity, I believe the details of the process have been incorrectly interpreted by Prof. Kenner. It is my belief that electron transference should be considered as a stabilizing factor in the transition state rather than the demanded reaction path.[2]

$$R-H \cdot X\cdot \longrightarrow \overset{\text{TRANSITION STATE}}{\left[\begin{matrix} R:H\,X\cdot & \leftrightarrow & R^{+}H\cdot X:^{-} & \leftrightarrow & R\cdot H- X:^{-} \\ \text{I} & & \text{II} & & \text{III} \end{matrix}\right]} \longrightarrow R\cdot + H-X$$

In terms of complete electron transference it is difficult to see why the relative reactivities of nuclear substituted toluenes or cumenes toward a free radical or atom should be dependent upon the structure of the radical or atom.

$$Y-C_6H_4-CH_3 + X\cdot \xrightarrow{k_2} Y-C_6H_4-CH_2\cdot + HX$$

According to the Kenner postulate the polar effect (the effect of the polar nature of Y on k_2) in the reactions of atoms and radicals which have a high electron affinity (e.g. Cl·, Br·) or a low electron affinity (e.g. $CCl_3\cdot$) should be equivalent. In actual fact an appreciable polar effect is observed for chlorine and bromine atoms (k_2 is reduced by electron-withdrawing substituents) whereas no polar effect has been detected in the reactions of trichloromethyl radicals.[3] In terms of resonance stabilization of the transition state these facts can be rationalized easily since the contribution of structure II should be most important when X· has the highest electron affinity.

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[1] J. Kenner, *Tetrahedron* 3, 78 (1958).

[2] G. A. Russell, *J. Amer. Chem. Soc.* **78**, 1047 (1956); F. R. Mayo and C. Walling, *Chem. Rev.* **46**, 191 (1950); C. Walling and E. A. McElhill, *J. Amer. Chem. Soc.* **73**, 2927 (1951).

[3] E. C. Kooyman, R. van Helden and A. F. Rickel, *Koninkl. Ned. Akad. Wetenschap. Proc.* **56B**, 75 (1953); R. van Helden and E. C. Kooyman, *Rec. Trav. Chim.* **73**, 269 (1954); C. Walling and B. Miller, *J. Amer. Chem. Soc.* **79**, 4181 (1957).

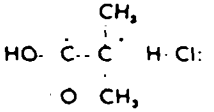
[4] G. A. Russell and H. C. Brown, *J. Amer. Chem. Soc.* **77**, 4578 (1955).

In terms of complete electron transference it would be expected that all atoms or radicals would remove the same hydrogen atom from a substrate containing a number of different carbon-hydrogen bonds. This is definitely not in accord with experimental observations.[4] For example, methyl radicals and chlorine atoms differ considerably in their point of attack on *iso*butyric acid. Methyl radicals attack the weakest carbon hydrogen bond of the molecule to yield the 3-alkyl radical predominately[5] whereas chlorine atoms attack mainly the β-hydrogen atoms.[6]

$$CH_3\cdot + (CH_3)_2CHCO_2H \longrightarrow CH_4 + (CH_3)_2\dot{C}CO_2H$$

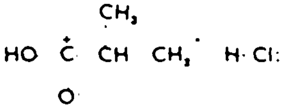
$$Cl\cdot + (CH_3)_2CHCO_2H \longrightarrow HCl + \cdot CH_2CH(CH_3)CO_2H$$

In terms of the stabilization of the transition state, resonance structure II would be expected to be more important for the chlorine atom than for the methyl radical because of the relative electron affinities of these species.[7] Thus abstraction of a hydrogen atom by a methyl radical proceeds *via* a transition state resembling III and product stability controls the point of attack. Stabilization of the transition state by II is not important because of the low electron affinity of the methyl radical. On the other hand the chlorine atom which has an extremely high electron affinity attacks the β-carbon-hydrogen bond of *iso*butyric acid, the bond having the highest electron density. The transition state for the attack of a chlorine atom upon the β-carbon-hydrogen bond can be stabilized by electron transference (II-β) whereas the transition state for attack at the α-carbon hydrogen bond would not be expected to be stabilized by electron transference because of the unfavorable adjacent charge in II-α.



$$\mathrm{HO{-}\underset{\cdot O}{\dot{C}}{\cdot\cdot}\overset{CH_3}{\underset{CH_3}{\dot{C}}}\;H{\cdot}Cl{:}}$$

II-α



$$\mathrm{HO\;\underset{O}{\overset{+}{C}}\;\overset{CH_3}{CH}\;\dot{C}H_2\;H{\cdot}Cl{:}}$$

II-β

Evidence for II as a contributing structure to the transition state for hydrogen abstraction has been furnished by the correlation of the relative reactivities of toluene and cumene derivatives toward various electrophilic atoms and radicals by means of Brown's σ^+-parameters.[8]

The finding of a linear free energy relationship between the rates of hydrogen abstraction from *meta- and para*-substituted toluenes and cumenes and the rates of hydrolysis of *meta- and para*-substituted dimethylbenzyl chlorides[9] suggests that both reactions involve transition states possessing similar stabilization. The similarity of resonance structure II for hydrogen abstraction and the transition state for the hydrolysis of dimethylbenzyl chlorides is apparent.

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[4] M. S. Kharasch and M. T. Gladstone, *J. Amer. Chem. Soc.* **65**, 15 (1943); C. C. Price and H. Morita, *Ibid.* **75**, 3686 (1953).

[5] A. Michael, *Ber.* **34**, 4028 (1901); M. S. Kharasch and H. C. Brown, *J. Amer. Chem. Soc.* **62**, 925 (1940).

[7] H. O. Prichard, *Chem. Rev.* **52**, 529 (1953).

[8] G. A. Russell, *J. Org. Chem.* **23**, 1407 (1958).

[9] H. C. Brown and Y. Okamoto, *J. Amer. Chem. Soc.* **79**, 1913 (1957); Y. Okamoto and H. C. Brown, *J. Org. Chem.* **22**, 485 (1957).