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COUPLING CONSTANTS AND REACTIVITIES IN ALIPHATIC SYSTEMS

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With the advent of extended-Huckel molecular orbital theories (1) and their application, via perturbation theory, to the rates of various reactions (2), it may become unnecessary to guess at transition states and factors affecting their energies, to the same extent as before (3). Unfortunately, molecular orbital theories tend to contain parameters which are adjusted to suit the situation, and this is why it is desirable to find theories which simply relate different properties of a molecule with each other. In this paper we hope to demonstrate a connection between reactivities and magnetic resonance spectra, at least in some particular cases.

Many reactions involve the loss of a group X from a molecule RX (e.g. loss of halide ion in the hydrolysis of alkyl halides) and this process may, or may not, be facilitated by the approach of a group Y_X to X and/or a group Y_R to some part of the fragment R-. As Y_X approaches X its charge/spin gets transferred to the fragment R- and in general, the greater the degree of transfer the weaker the R-X bond becomes. If this bond is stretched in the transition state then we expect that the more easily R- can accommodate the appropriate charge or spin, initially associated with Y_X, the lower will be the activation energy of a reaction in which X is lost. The chief factor assisting in this transference of charge/spin from Y_X, in the cases we shall consider, is the degree of delocalisation in the fragment R-(4).

Very often we can obtain a good description of the R-X bond by considering only the interaction between the approximately non-bonding orbital of R- and a single molecular/atomic orbital of X. The distribution of 'extra' charge or spin arising from the R-X...Y_x interaction, is then approximately the same as that of spin in the radical R-; i.e. according to simple molecular orbital theory. Now the spin distribution in R- is something we could measure, in principle, from the hyperfine splittings in its E.S.R. spectrum, but in practice the free radical R has the wrong geometry. However, it has been shown (5a) that the electron-nuclear hyperfine interactions in these unstable radicals R- are proportional to the coupling constants of H*, observed in the N.M.R. spectrum of RH*, as long as the nuclei in question are separated from H* by an odd number of bonds.

We can therefore expect the following relationship:- The larger the coupling constant $J_{H^*-CH_3}$ in $H^*CR_2CH_3$, the less the total delocalisation in the fragment $-CR_2CH_3$ and the larger the activation energy of a process; $Y_x + XCR_2CH_3 = Y_x.X$ + products (X, Y_x may be charged).

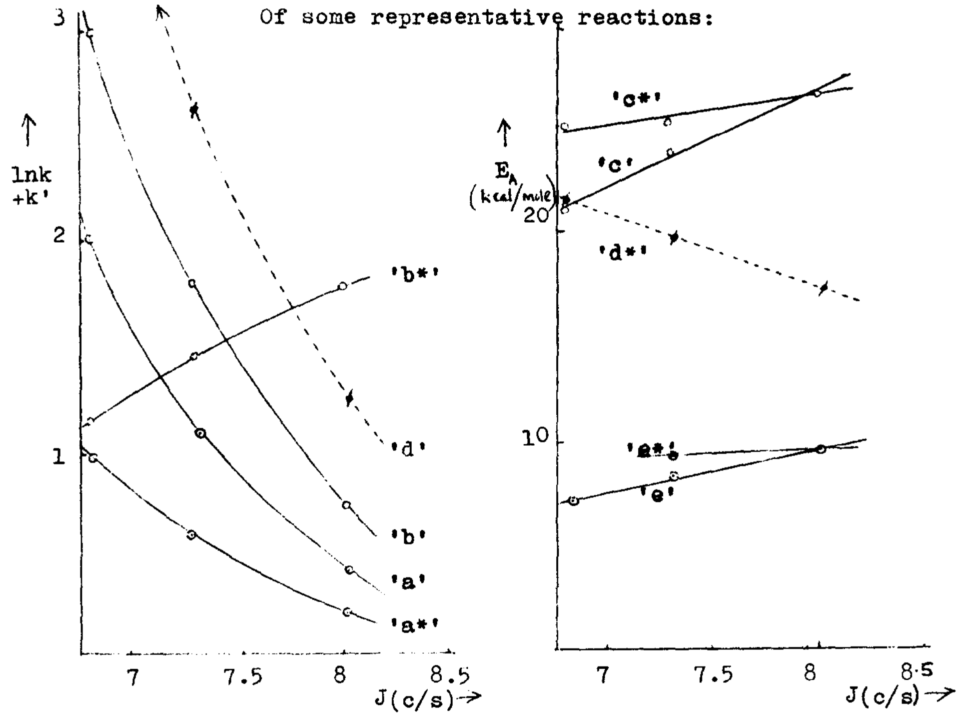
The vicinal proton spin-spin coupling constants in the simple alkanes are:- CH_3CH_3, 8c/s; $(CH_3)_2CH_2$, 7.3c/s; $(CH_3)_3CH$, 6.8c/s;(6) and so the ease of loss of X should increase in the order: primary $<$ secondary $<$ tertiary, and this is the case for E2, E1, S_N1, E1cB and radical abstraction reactions but not for S_N2 reactions when the reverse applies (see FIG. I)

A similar order of reactivity would be expected when a nucleophile Y_R attacks a hydrogen in R-(5b), and this is found to be so in concerted Saytzeff-type eliminations but not in the Hoffman-type, implying that only stretching of the R-X bond is important in the latter case, when the complexity of the departing group has to be taken into account.

From the order of reactivity in S_N2 reactions, it would appear that direct interactions (repulsions) of the α-methyl groups with

FIG. I

Empirical relationship between coupling constants and rates Of some representative reactions:



J = vicinal methyl proton coupling constant, either as measured or as estimated in compounds (i) $\overset{\frown}{CH_3\underset{\alpha}{C}}HRR'$, for curves a,b,c,d,d*,e - which illustrate the effects of α-substituents on the rates of reactions of $CH_3CRR'X$; (ii) $\overset{\frown}{\underset{\beta}{C}HRR'\underset{\alpha}{C}H_3}$, for curves a*,b*,c*,e*,- which show the effects of β-substituents in reactions of $\underset{\beta}{C}HRR'\underset{\alpha}{C}H_2X$.

k= rate constant, k'= constant for each curve, E_A = activation energy.

a, a* :- E2, $\overset{-}{O}Et$ catalyst, $RBr \rightarrow$ olefin (3) - Saytzeff-type

b, b* :- E2, $\overset{-}{O}Et$ catalyst, $R\overset{+}{S}Me \rightarrow$ olefin (3) - Hoffman-type

c, c* :- E1, gas phase, $RBr \rightarrow$ olefin (7) - Saytzeff-type

e, e* :- Radical abstraction, $\frac{1}{2}RH + \frac{1}{2}CH_3 \rightarrow \frac{1}{2}R\cdot + \frac{1}{2}CH_4$ (4)

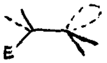
d :- S_N1, $RBr + \overset{-}{OH} \rightarrow ROH + \overset{-}{Br}$ (3)

d* :- S_N2, $RBr + {}^*\overset{-}{Br} \rightarrow R^*Br + \overset{-}{Br}$ (3)

Y_X = solvent (?) for a,b,d; β-H for c.

Y_R = $\overset{-}{O}Et$ for a,b; $\overset{-}{OH}$ for d; $\overset{-}{Br}$ for d*; α-Br for c.

the incoming nucleophile are sufficient to offset their rather feeble delocalising (hyperconjugative) power, i.e. rate is determined by the ease of approach of Y_R.

Rates of addition reactions may similarly be connected with N.M.R./E.S.R. coupling constants by considering them as the reverse of eliminations; i.e. the initial step is addition of an electrophile or radical, E, to give a species somewhere between the π-complex  and the σ-fragment allowing maximum delocalisation  . Hence we expect this initial addition to be such that the most favourable ion/radical is formed; usually this means that the electrophile/radical adds to the carbon attached to the largest number of hydrogens.

e.g. Addition to $(\overset{1}{C}H_3)_2\overset{a}{C}=\overset{b}{C}H\overset{2}{C}H_3$

In molecule: $(\overset{1}{C}H_3)_2\overset{a}{C}H.\overset{b}{C}H_2\overset{2}{C}H_3$, $J_{a1} \approx 6.8$ c/s, $J_{b2} \approx 7.3$ c/s, therefore initial addition is to carbon atom 'b'. This accounts for Markownikoff's rule and the direction of radical addition of HBr.

The stereochemistry of addition/elimination reactions may be correlated with splittings in magnetic resonance spectra in a similar manner.

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