

[CONTRIBUTION FROM THE GENERAL ELECTRIC RESEARCH LABORATORY]

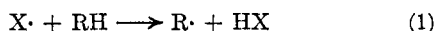
## Nature of the Polar Effect in Reactions of Atoms and Radicals<sup>1</sup>

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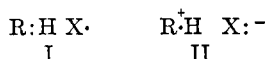
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Evidence is presented that the transition state for the attack of bromine atoms or *N*-succinimidyl radicals on benzyl hydrogen atoms involves charge separation (e.g.  $R^{\cdot}H^{\oplus} X^{\ominus}$ ). For the more reactive chlorine atom, the transition state involves little breaking of the carbon-hydrogen bond and charge separation does not appear to be important.

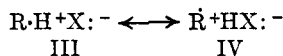
Polar effects have been observed in the attack upon carbon-hydrogen bonds of bromine atoms,<sup>2</sup> chlorine atoms,<sup>3</sup> peroxy radicals,<sup>4</sup> and *N*-succinimidyl radicals.<sup>2</sup> When  $X^{\cdot}$  has a high electron affinity,



electron-withdrawing groups decrease reactivity while electron-supplying groups increase reactivity. It has been suggested that, depending upon the reactivity and electron affinity of  $X^{\cdot}$ , the transition state can vary between structures I and II.<sup>3c,4,5</sup> Structure II can be considered to be a resonance



hybrid of structures III and IV.



When  $X^{\cdot}$  is extremely reactive, there will be little breaking of the carbon-hydrogen bond and the tran-

sition state will resemble the reactants (structure I).<sup>6</sup> The stability of I (as R is varied) may depend upon the electron density of the carbon-hydrogen bond, at least when  $X^{\cdot}$  has a high electron affinity. The energy content may be proportional to a weak electrostatic interaction between  $X^{\cdot}$  and the electrons of the carbon-hydrogen bond, possibly best expressed in terms of a repulsion curve.<sup>6b</sup>

As the reactivity of  $X^{\cdot}$  decreases, the amount of bond-breaking in the transition state will increase and the transition state will be more nearly described by structures III and IV. Structure IV, which involves charge separation, also predicts the observed polar effect.

These two possible interpretations of the polar effect, one based on considerations of the electron density of the carbon-hydrogen bond and one based on the ability of R to accommodate a positive charge, lead to different predictions in regard to the effects of *m*- and *p*-substituents upon the reactivity of toluene. If the electron density of the  $\alpha$ -carbon-hydrogen bond determines reactivity, then the substituent effect should be correlated by the  $\sigma$ -constants calculated from the acidity of substituted benzoic acids.<sup>7</sup> If, however, the polar effect is a manifestation of the resemblance of the transition state to II, then the effects of substituents should be

(1) Directive Effects in Aliphatic Substitutions. Part XIV. For Part XIII see *J. Am. Chem. Soc.*, **80**, 5002 (1958).

(2) E. C. Kooyman, R. van Helden, and A. F. Bickel, *Koninkl. Ned. Akad. Wetenschap. Proc.*, **56B**, 75 (1953).

(3) (a) R. van Helden and E. C. Kooyman, *Rec. trav. chim.*, **73**, 269 (1954); (b) H. C. Brown and A. B. Ash, *J. Am. Chem. Soc.*, **77**, 4019 (1955); (c) G. A. Russell and H. C. Brown, *J. Am. Chem. Soc.*, **77**, 4578 (1955); (d) C. Walling and B. Miller, *J. Am. Chem. Soc.*, **79**, 4181 (1957).

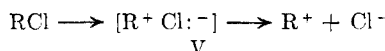
(4) C. Walling and E. A. McElhill, *J. Am. Chem. Soc.*, **73**, 2927 (1951); G. A. Russell, *J. Am. Chem. Soc.*, **78**, 1047 (1956).

(5) F. R. Mayo and C. Walling, *Chem. Revs.*, **46**, 191 (1950).

(6) (a) G. S. Hammond, *J. Am. Chem. Soc.*, **77**, 334 (1955); (b) M. G. Evans and M. Polanyi, *Trans. Faraday Soc.*, **34**, 11 (1938).

(7) (a) L. P. Hammett, *Physical Organic Chemistry*, McGraw-Hill Book Co., Inc., New York, N.Y., 1940, Ch. VII; (b) D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, **23**, 420 (1958).

determined by the  $\sigma^+$ -constants obtained, for example, from the rates of hydrolysis of dimethylbenzyl halides.<sup>8</sup> This conclusion is based on the similarity between IV and the transition state V for the hydrolysis of a tertiary benzyl chloride.



Suitable data are available to test these ideas. Kooyman has reported the relative reactivity of a number of toluene derivatives towards *N*-succinimidyl radicals and bromine atoms,<sup>2</sup> both relatively unreactive radicals which should give rise to transition states involving considerable bond breaking. In Figs. 1 and 2 the relative reactivities have been plotted as a function of the  $\sigma$ -constant derived from the ionization of benzoic acids.<sup>7b</sup> *p*-Methoxytoluene has an unusually high reactivity in both reactions.<sup>9</sup> In Figs. 1 and 2 the relative reactivities have also

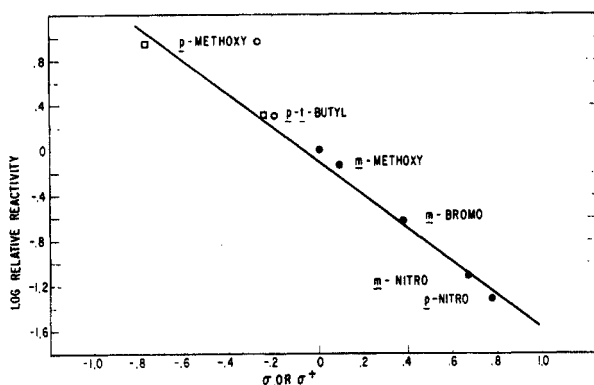


Fig. 1. Correlation between log relative reactivity and  $\sigma^+$  for attack of *N*-succinimidyl radicals upon substituted toluenes at 80°;  $\square$ ,  $\sigma^+$ ;  $\circ$ ,  $\sigma$ ;  $\bullet$ ,  $\sigma = \sigma^+$ . Log relative reactivity =  $-1.5\sigma^+$

been plotted as a function of  $\sigma^+$ -constants. The reactivity of *p*-methoxytoluene is no longer anomalous. On the basis of the arguments given previously, it is concluded that the polar effects in these reactions result because of the resemblance between the transition state and structure IV.<sup>10</sup>

The attack of a chlorine atom upon a carbon-hydrogen bond has been described as one which involves very little bond-breaking and should resem-

(8) (a) H. C. Brown and Y. Okamoto, *J. Am. Chem. Soc.*, **79**, 1913 (1957); (b) Y. Okamoto and H. C. Brown, *J. Org. Chem.*, **22**, 485 (1957); (c) N. C. Deno and W. L. Evans, *J. Am. Chem. Soc.*, **79**, 5804 (1957); (d) N. N. Lichtin and H. P. Leftin, *J. Phys. Chem.*, **60**, 64 (1956).

(9) The Hammett  $\sigma$ -constants are not a true measure of the inductive effect of a substituent of an aromatic ring and therefore, in cases where resonance effects are unimportant, will not give a true picture of the electron density of  $\alpha$ -carbon-hydrogen bonds. The  $\sigma_I$ -parameters (see footnote 22, ref. 8b) of Taft [R. W. Taft, Jr., in M. S. Newman, ed., *Steric Effects in Organic Chemistry*, John Wiley and Sons, New York, Ch. 13], which are a measure of the inductive effect of a substituent, give a very poor fit with the data of Figs. 1 and 2, mainly because the  $\sigma_I$ -constant for a methoxy group is positive.

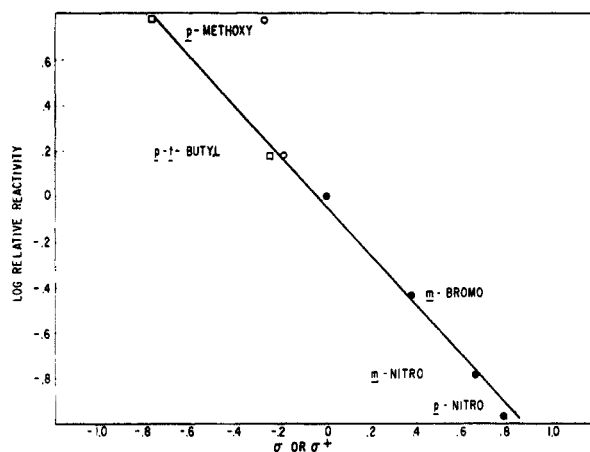


Fig. 2. Correlation between log relative reactivity and  $\sigma^+$  for the attack of bromine atoms upon substituted toluenes at 80°;  $\square$ ,  $\sigma^+$ ;  $\circ$ ,  $\sigma$ ;  $\bullet$ ,  $\sigma = \sigma^+$ . Log relative reactivity =  $-1.1\sigma^+$

ble I.<sup>3c</sup> Therefore, it is not surprising that the relative reactivities of *p*- and *m*-substituted toluenes determined by Walling and Miller<sup>3d</sup> and by van Helden and Kooyman<sup>3a</sup> are better correlated by  $\sigma$  than by  $\sigma^+$ . The relative reactivities of toluene, *m*-xylene, *m*-phenyltoluene, *m*-chlorotoluene, *p*-toluic acid, *m*-tolunitrile, and *p*-tolylmethylsulfone, reported by these workers, yield the expression

$$\text{Log relative reactivity} = 0.06 - 1.25\sigma \quad (2)$$

with a standard deviation (root mean square) of 0.058 log unit (on the basis of  $\sigma$ -constants given in ref. 7b). This relationship is plotted in Fig. 3. All of the substituents used in the determination of (2) have equivalent  $\sigma$ - and  $\sigma^+$ -constants. It is, there-

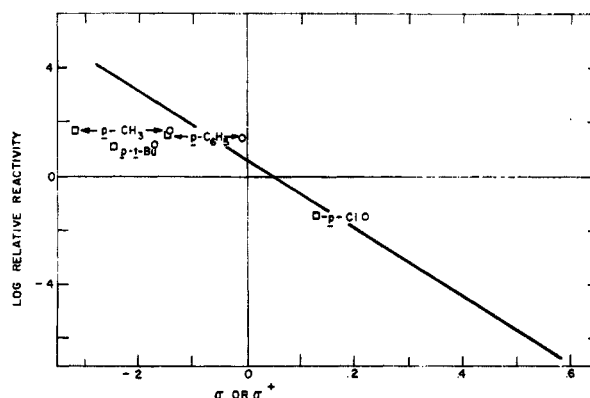
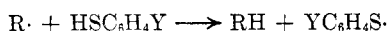


Fig. 3. Correlation between log relative reactivity and  $\sigma$  for the attack of chlorine atoms upon substituted toluenes at 70°;  $\square$ ,  $\sigma^+$ ;  $\circ$ ,  $\sigma$ . Log relative reactivity =  $0.06 - 1.25\sigma$

(10) Since the  $\sigma^+$ -parameters involve important resonance stabilization (of benzyl-type cations), it might be argued that they could also reflect differences in the resonance stabilization of incipient benzyl radicals in the transition state (III). However, it is difficult to imagine why resonance stabilization should be the same for free radical and cationic intermediates, particularly in the case of substituents such as *p*-nitro. It thus appears that resonance stabilization of the incipient benzyl radical is either constant or unimportant in these reactions.

fore, of interest to compare the effect of four more substituents, whose  $\sigma^-$  and  $\sigma^+$ -constants are not equivalent, with (2). Fig. 3 gives the experimental points for *p*-chloro, *p*-*t*-butyl, *p*-phenyl and *p*-methyl substituents on the basis of both  $\sigma^-$  and  $\sigma^+$ -constants. On the basis of  $\sigma^-$ -constants, the total deviation for the four points is 0.40 log unit. On the basis of  $\sigma^+$ -constants, the deviation is 0.60 log unit. Moreover, all of the deviations for  $\sigma^+$ -constants are negative while for  $\sigma^-$ -constants two deviations are positive (*p*-chloro, *p*-phenyl) and two are negative (*p*-*t*-butyl, *p*-methyl). The total negative deviations are 0.21 log unit while the positive deviations total 0.19 log unit. Recalculation of the best straight line using the four additional points and their  $\sigma^-$ -constants, yields the equation, log relative reactivity =  $0.06 - 1.23 \sigma^-$ , with a standard deviation of 0.085 log unit. It thus appears that the transition state for the attack of a chlorine atom upon a benzyl hydrogen atom is best represented by I and not by II, although the need for more data, particularly in regard to *p*-alkoxytoluenes, is evident.

Similarly, the reaction of the 1-cyano-1-cyclohexyl radical with substituted thiophenols

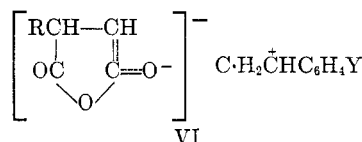


gives excellent agreement with  $\sigma^-$ -constants, even with the *p*-methoxy substituent.<sup>11</sup> Here structure IV (with R =  $\text{YC}_6\text{H}_4\text{S}$ ) would be quite unstable because of the unfavorable charge separation, and the polar effect is best explained by a consideration of structure I.

Further examples of polar effects in the reactions of free radicals are furnished by the addition of

(11) Y. Schaafsma, A. F. Bickel, and E. C. Kooyman, *Rev. trav. chim.*, **76**, 180 (1957).

radicals to olefins. A pronounced polar effect has been found in the reactions of radicals with a high electron affinity with substituted styrenes. For example, a polymer radical terminating in a maleic anhydride unit would be expected to have a high electron affinity because of the stability of the corresponding anion. It has been suggested that the reaction of a polymeric maleic anhydride radical with styrene would be expected to involve transition state stabilization similar to VI.<sup>5</sup>



Again the importance of VI in the transition state should be a function of the  $\sigma^+$ -parameters of Y whereas the electron density of the double bond of styrene should more closely parallel  $\sigma^-$ -parameters. Support for VI is found in the conclusion that the relative reactivities of a number of substituted  $\alpha$ -methylstyrenes towards polymeric maleic anhydride radicals or *S*-thioglycolic acid radicals, are better correlated by  $\sigma^+$ -constants than by  $\sigma^-$ -constants.<sup>12</sup>

SCHENECTADY, N. Y.

(12) Pertinent data are summarized in ref. 5. For this correlation a  $\sigma^+$ -parameter for the *p*-dimethylamino group is necessary. From the results summarized by Deno and Evans (ref. 8c) an average value of  $-1.70$  is indicated. Mayo and Walling (ref. 5) discuss the serious deviation of plots using  $\sigma^-$ -constants and point out that the deviations are similar to those observed in the hydrolysis of benzhydryl or triaryl-methyl chlorides.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PRESBYTERIAN COLLEGE]

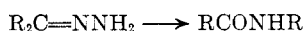
## The Rearrangement of the Stereoisomeric Camphorquinone-3-hydrazones

K. N. CARTER

April 30, 1958

The *syn*- and *anti*-camphorquinone-3-hydrazones have been rearranged to  $\alpha$ -camphoramic acid by means of sodium nitrite and concentrated sulfuric acid. Isomer interconversion was found to occur under the influence of concentrated sulfuric acid alone. The rearrangement results have been interpreted on the basis of *anti*-migration. A possible mechanism is suggested. The similarity of the rearrangement to the second type Beckmann is noted.

The rearrangement of hydrazones to amides



discovered by Pearson and Greer<sup>1</sup> when applied to the stereoisomeric hydrazones<sup>2</sup> of *p*-methoxybenzo-

(1) D. E. Pearson and C. M. Greer, *J. Am. Chem. Soc.*, **71**, 1895 (1949).

(2) D. E. Pearson, K. N. Carter, and C. M. Greer, *J. Am. Chem. Soc.*, **75**, 5905 (1953).

phenone and *p*-bromobenzophenone gave results which allowed structures to be assigned based on the assumption of *anti*-migration as is known to occur in the Beckmann rearrangement of oximes. The present work is a study of the rearrangement behavior of the stereoisomeric camphorquinone-3-hydrazones whose structures were already known.

The *syn*- and *anti*-isomers of camphorquinone-3-hydrazone were prepared and well characterized