Tetrahedron Letters No. 25, pp 2183 - 2186, 1976. Pergamon Press. Printed in Great Britain.

INDUCTIVE, CC-HYPERCONJUGATIVE AND FRANGOMERIC EFFECTS IN THE SOLVOLYSIS OF 1-SUBSTITUTED 3-BROMOADAMANTANES

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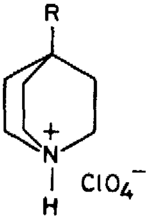
(Received in UK 26 April 1976; accepted for publication 10 May 1976)

Three kinds of polar substituent effects are discernible in the solvolyses of 1-R-substituted 3-bromoadamantanes (2) in 80 % ethanol. This follows from the reaction products and from the relationship between the logarithms of the first order rate constants (log k) and the respective inductive substituent constants σ_I^q. The latter were derived recently from the pK_a values of 4-R-substituted quinuclidinium perchlorates (1) according to the equation $pK_a^H - pK_a^R = \rho \sigma_I^q$ [1].



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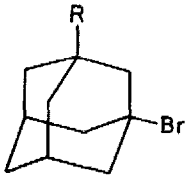

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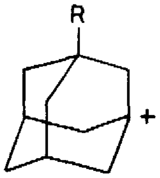

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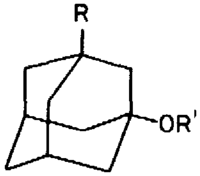


4 a) R' = H
b) $R' = C_2H_5$

The first group of bromides 2, i.e. R = H, CH_3, C_2H_5, $i\text{-}C_3H_7$, CH_2Br, COOH and Br, yield only the alcohols and ethers 4a and 4b by the unimolecular substitution mechanism (S_N1) which involves the carbenium ions 3 as intermediates. The log k values correlate well with the respective σ_I^q values (correlation coefficient 0,998) as shown in the Figure. Therefore, in these cases ionisation rates are determined only by the inductive effect of R.

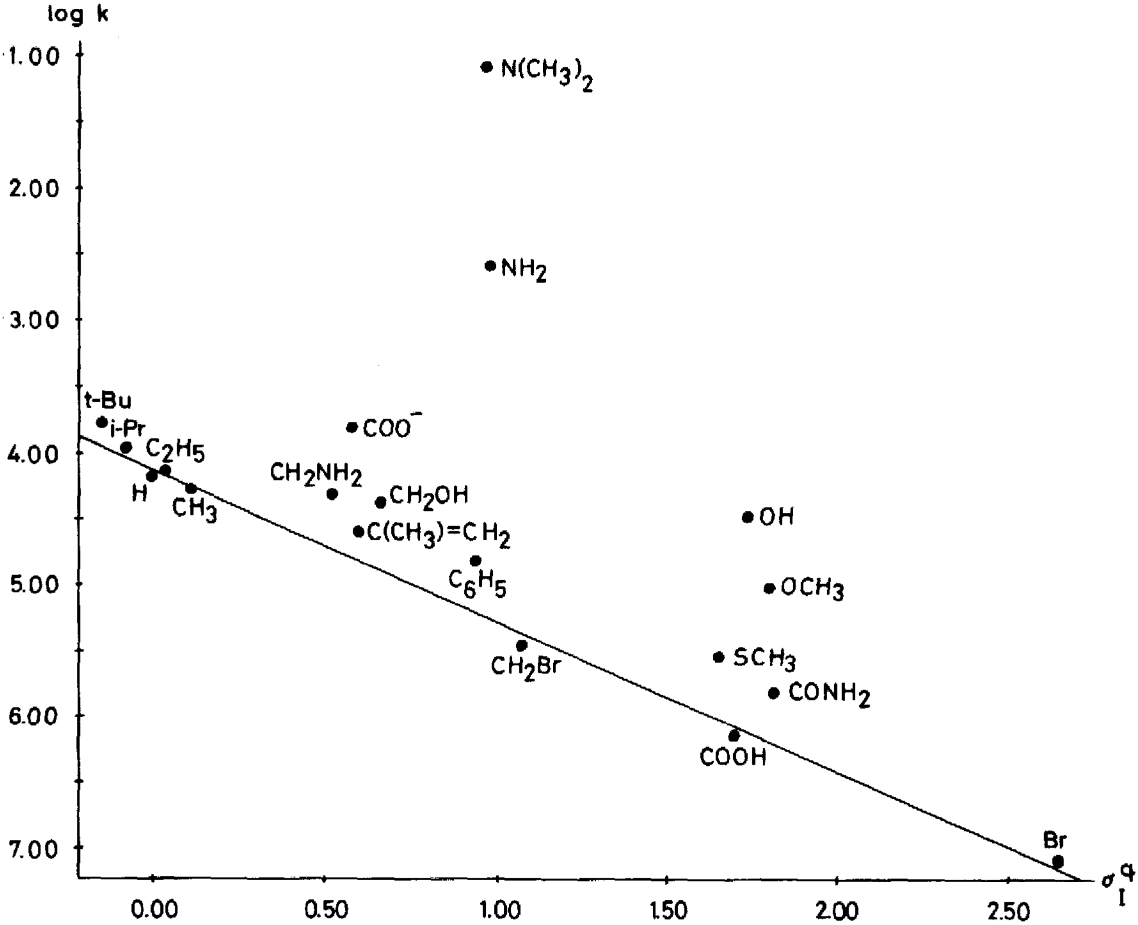
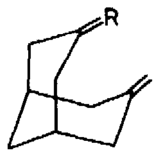


Figure. Plot of log k of 1-R-substituted 3-bromoadamantanes (2) in 80 vol. % ethanol at 70,0° C against σ_I^q values.

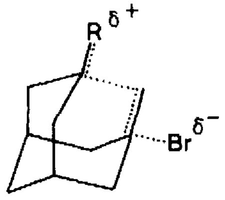


R =

5a $^+NH_2$

5b $^+N(CH_3)_2$

5c O



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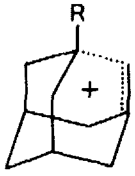

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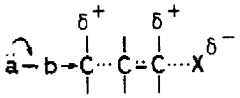
On the other hand the bromides 2 with R = NH_2 and $N(CH_3)_2$ undergo quantitative fragmentation to the imonium ions 5a and 5b and their rate constants are 4.7×10^2 and 1.5×10^4 times, respectively, as fast as those calculated on the basis of the regression line in the plot. As shown previously [2] ionization of these compounds is accompanied by the cleavage of the C(1)-C(2) bond and assisted by the frangomeric effect [3] of the amino groups as illustrated in 6.

3-Bromoadamantanol (2) (R = OH) is marginal in that it reacts 44 times as fast as calculated from the σ_I^q value of the hydroxy group. Nevertheless, it undergoes 30 % substitution to 4a and 4b (R = OH) beside 70 % fragmentation to 5c. The formation of the substitution products by concerted fragmentation and subsequent recyclization of the unsaturated ketone 5c to the cation 3 (R = OH) is unlikely under the reaction conditions, i.e. in the presence of 1 to 4 equivalents of triethylamine, since the base does not effect the rate and the product composition [4]. It can therefore be concluded that in this case concerted fragmentation (70 %) to 5c competes with ionization to the cation 7 (R = OH) (30 %), in which the positive charge is partially transferred to C(1) by delocalization of the C(1)-C(2) bond, i.e. by CC-hyperconjugation. This kind of σ-bond delocalization, which leads to heterolytic fragmentation in extreme cases [5], has been postulated to occur in solvolysis reactions [6]. However, experimental evidence has hitherto been lacking.

The remaining bromides (2) included in the plot react 1.5 to 15 times faster than expected on the basis of the σ_I^q values of the substituents R. Of these the $C(CH_3)=CH_2$, C_6H_5, SCH_3 and OCH_3 groups are capable of stabilizing the partial positive charge generated at C(1) in the cation 7 by delocalization of their π- or p-electrons. On the other hand, the rate-enhancing role of the t-Bu, CH_2OH, CH_2NH_2, $CONH_2$ and COO^- groups is not so evident at first. A common trait, however, is that they are potentially electrofugal groups a-b when combined with a middle group c-d and a nucleofuge X, as illustrated in the generalized fragmentation scheme [5]:

$$\text{a-b-c-d-X} \longrightarrow \text{a-b}^+ + \text{c=d} + \text{X}^-$$

They should therefore also act as mild electron donors when hyperconjugated with an incipient positive reaction center, as in the transition state 8 leading to the cation 7.



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It is evident from the plot that the CC-hyperconjugative and frangomeric effects of substituents more or less counterbalance their inductive effects. Moreover, their contributions to the total polar substituent effect appear to vary continuously.

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2) C.A. Grob & W. Schwarz, ibid. 47, 1870 (1964).

3) C.A. Grob, Angewandte Chemie 81, 543 (1969), internat. edit. 8, 535 (1969).

4) Cyclization of 5c to 4a and 4b (R = OH) does, however, occur in acidic solution.

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