A Hammett Correlation for the Rates of Diels–Alder Reactions of 2-Substituted Butadienes

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Summary A comparison of two sets of data on the relative rates and isomer ratios of Diels–Alder reactions of 2-substituted butadienes with methyl acrylate and with the methyl acrylate–aluminium chloride complex reveals an excellent Hammett correlation with σ^+.

ALTHOUGH Hammett correlation for Diels–Alder reactions has been reported,[1] the substituent changes were confined to those directly on the benzene ring either of the dienes or dienophiles, except[2] where the substituents were introduced on the diene or dienophile functions. A four-parameter equation was presented[2] to correlate the sets of observed rate data, which are sometimes the average of rates of formation of isomeric products.

We report that a simple two-parameter ($p\sigma^+$) correlation is obtained when the "partial rate factors" of formation of isomers from 2-X-butadienes (X = Me, Ph, Cl, CF_3, and CN) and methyl acrylate are compared with the corresponding data with the methyl acrylate–aluminium chloride complex as the dienophile[3] (Equation 3).

The isomer distribution of the products (p : m ratio) and relative rates, 2-X-butadiene as opposed to butadiene, at 20° in benzene were determined in a way similar to that described previously,[4] and the observed partial rate factors (p.r.f.) were calculated by somewhat artificially assigning the "p" and "m" products to the action of the β-carbon of the dienophile at the 1- and 4-positions of the dienes, respectively. The p.r.f.$^{(u)}$ for the uncatalysed (methyl acrylate) reaction and p.r.f.$^{(c)}$ for catalysed (methyl acrylate–$AlCl_3$) reaction are listed in the Table.

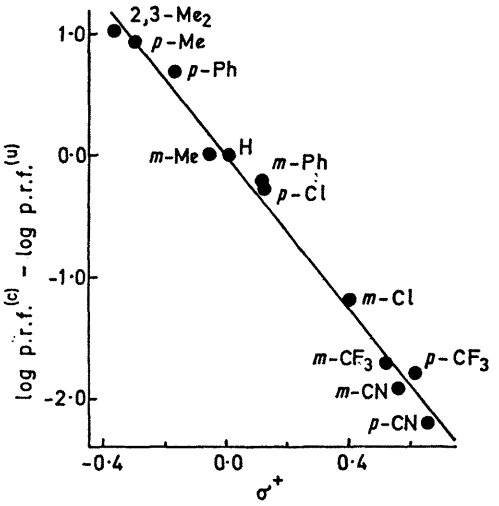
Partial rate factors at 20°[a]

X	p.r.f.$^{(c)}$ 1—	p.r.f.$^{(c)}$ 4—	p.r.f.$^{(u)}$ 1—	p.r.f.$^{(u)}$ 4—
CH_3	23·0	1·20	2·68	1·15
Ph	183	5·67	37·0	9·2
Cl	1·08	0·02	2·07	0·309
CF_3	0·326	0·314	19·5	15·9
CN	0·147	0·055	23·2	4·42
2,3-Me_2	36·2	36·2	3·43	3·43

[a] Reactivity of one terminal carbon of unsubstituted butadiene is taken as unity for each set of p.r.f.'s; note that the actual rate constants for the catalyzed reactions are 10^5 times as large as those for the corresponding members of the uncatalysed reactions.[3]

The observed p.r.f. is related to the reactivities (k) of the pertinent positions of the dienes (based on a normalized concentration of s-*cis* conformers through which the Diels–Alder reaction proceeds) (Equation 1), K's are

$$\begin{aligned} \text{p.r.f.}^{(u)} &= (k^X/k^H)^{(u)}\ K^X(K^H + 1)/[K^H(K^X + 1)] \\ \text{p.r.f.}^{(c)} &= (k^X/k^H)^{(c)}\ K^X(K^H + 1)/[K^H(K^X + 1)] \end{aligned} \quad (1)$$



Hammett plot: σ_p^+ *for* 1-*position and* σ_m^+ *for* 4-*position*: $\sigma_{p\text{-Me}}^+ + \sigma_{m\text{-Me}}^+$ *for* 2,3-*dimethylbutadiene* (*designated by* 2,3-Me).

[1] See ref. 2 and references therein.
[2] M. Charton, *J. Org. Chem.*, 1966, **31**, 3745.
[3] T. Inukai and T. Kojima, *J. Org. Chem.*, 1967, **32**, 872.
[4] T. Inukai and T. Kojima, *J. Org. Chem.*, 1966, **31**, 1121.

the equilibrium constants for s-*trans* ⇌ s-*cis*). The ratio $k^X : k^H$ cannot be evaluated since the K-values are unknown. Hence a correlation is obtained in the form of Equation 2, eliminating the unknowns by side-by-side division. The Figure shows the Hammett plot according to

$$\text{p.r.f.}^{(c)}/\text{p.r.f.}^{(u)} = (k^X/k^H)^{(c)}/(k^X k^H)^{(u)} \quad (2)$$

$$\log \text{p.r.f.}^{(c)} - \log \text{p.r.f.}^{(u)} = \rho\sigma^+ \quad (3)$$

Equation 3 where $\rho = -3{\cdot}12$ ($r = 0{\cdot}994$, $s = 0{\cdot}129$).

It can be shown from the isomer ratios that Equations 4 and 5 do not hold under the conditions of Equation 3.

$$\log (k^X/k^H)^{(u)} = \rho^{(u)}\sigma^+ \quad (4)$$

$$\log (k^X/k^H)^{(c)} = \rho^{(c)}\sigma^+ \quad (5)$$

Therefore, although each set of data with a dienophile (Equation 4 or 5) does not follow the Hammett correlation, the change of k^X/k^H due to the change of the dienophile character is linearly dependent on σ_X^+.

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