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THE RELATIVE RATES OF ADDITION OF CYANOETHYLENES TO ANTHRACENE AND ITS 9-DEUTERIO- AND 9,10-DIDEUTERIO-DERIVATIVES

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Abstract—In a range of solvents of widely varying dielectric constants tetracyanoethylene adds to anthracene about 90% as fast as to 9, 10-d$_2$-anthracene. In ethanol the adduct with deuterium on the bridgehead carbon atoms dissociates 85% as fast as the undeuteriated adduct, indicating that in the transition state the hybridization of C_9 and C_{10} is nearer to sp^2 than sp^3.

The 7% preference for addition of C_9 to C_β over C_α in the reaction of 9-d-anthracene with acrylonitrile and methylenemalononitrile shows that in the transition state of these unsymmetrical Diels-Alder reactions the new bond is more formed at the more electrophilic end of the dienophile's double bond. The same preference in the reaction with the more symmetrical tricyanoethylene and tricyanovinyl chloride was barely outside the experimental error.

To compliment a study of the effect of solvent on the kinetics of addition of tetracyanoethylene to anthracene[1] we have measured the effect of substitution of deuterium on the carbon atoms to which the new bonds are formed.[2]

While it may not be clear in a particular case how much the secondary α-deuterium isotope effect,[3] arising from the reduction in out of plane bending frequency of the α-proton as the carbon atom rehybridizes[4a] from sp^3 to sp^2, is modified by changes in non-bonded repulsions[5] or ground-state differences between C—H and C—D bonds,[6] it is an empirical fact that several reactions in which (sp^3)C—H changes to (sp^2)C—H (e.g. S$_N$1 solvolysis,[4a,b] loss of nitrogen from azo-compounds[4c]) the normal compound reacts about 12–15% faster than the α-monodeuterio-derivative at ordinary temperature.[3] A difference of similar magnitude in the opposite direction (D faster than H) is often found for reactions where the change is sp^2 $\rightarrow$ sp^3 (e.g. addition to olefins).[4d]

The rate constants quoted in Table 1 are each the mean of 8 to 10 separate runs, every rate plot having at least 9 points (as detailed in Ref. 1). The differences in the

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[1] P. Brown and R. C. Cookson, *Tetrahedron* **21**, 1977 (1965).

[2] P. Brown and R. C. Cookson, *Abstracts Papers A.C.S. Meeting* P.7U. Chicago, September (1964).

[3] For a recent review of secondary deuterium kinetic isotope effects see E. A. Halevi in *Progress in Physical Organic Chemistry* Vol. 1. Interscience, New York (1963).

[4] [a] A. Streitwieser, R. H. Jagow, R. C. Fahey and S. Suzuki, *J. Amer. Chem. Soc.* **80**, 2326 (1958); [b] R. R. Johnson and E. S. Lewis, *Proc. Chem. Soc.* 52 (1958); [c] S. Seltzer, *J. Amer. Chem, Soc.* **83**, 2625 (1961); **85**, 14 (1963); [d] D. B. Denney and N. Tunkel. *Chem. & Ind.* 1383 (1959); M. Matsuoka and M. Swarc, *J. Amer. Chem. Soc.* **83**, 1260 (1961); S. Seltzer, *Ibid.* **83**, 1861 (1961); M. Takahashi and R. J. Cvetanovic, *Canad. J. Chem.* **40**, 1037 (1962); M. Feld, A. P. Stefani and M. Swarc, *J. Amer. Chem. Soc.* **84**, 4451 (1962).

[5] L. S. Bartell. *Tetrahedron Letters* 13 (1960); *J. Amer. Chem. Soc.* **83**, 3567 (1961); for examples see K. Mislow, R. Graeve, A. J. Gordon and G. H. Wahl, *Ibid.* **85**, 1199 (1963); and L. Melander and R. E. Carter, *Ibid.* **86**, 295 (1964).

[6] E. A. Halevi, *Tetrahedron* **1**, 174 (1957); E. A. Halevi, M. Nussim and A. Ron, *J. Chem. Soc.* 866, 876 (1963).

change in free energy for the 9,10-H_2 and D_2 reactions, given in the last column, were calculated from the expression

$$\Delta(\Delta F) = 2 \cdot 303 \frac{RT}{n} \log \frac{k_H}{k_D}$$

where n is the number of α-deuterium atoms per molecule (1·797 by analysis). Although the variation of k_H/k_D and $\Delta\Delta F$ with change in solvent seems to be outside the experimental error, it does not correlate with solvent polarity, k_H, $\Delta H^{\ddagger}$ or $\Delta S^{\ddagger}$. Its relative constancy is expected from the rather small sensitivity of rate to solvent,[1] implying approximately the same change in hybridization at C_9 and C_{10} at the transition state in all solvents. If the isotope effect k_H/k_D for addition in ethanol is assumed to be the same as in the other solvents (about 0·90), then the significantly larger effect ($k_D/k_H = 0 \cdot 85$) for the dissociation in ethanol must indicate a greater change in hybridization of C_9 and/or C_{10} in going from the adduct to the transition state than from the transition state to the addends. For the forward Diels-Alder reaction this would agree with the picture of the reaction's proceeding by isomerization of the π-complex into the adduct[1] through a transition state resembling the π-complex more than the adduct.

As a means of probing the mechanism of a cyclic reaction between two symmetrical addends, such as anthracene and tetracyanoethylene, di-deuteriation of one addend (e.g. C_9 and C_{10}) suffers from a serious inherent ambiguity: a particular degree of rehybridization of both C_9 and C_{10} (i.e. a symmetrical transition state) cannot be distinguished from a greater degree of rehybridization at C_9 and correspondingly less at C_{10} (i.e. an unsymmetrical transition state), or the extreme of all rehybridization at C_9 and none at C_{10} (i.e. a transition state leading to a dipolar intermediate held in conformational rigidity by electrostatic attraction or intramolecular charge-transfer).*

This problem does not arise, of course, for reactions where one of the addends is unsymmetrical and the other is symmetrical and monodeuteriated.[7,8] 9-d-Anthracene was added to cyano-, 1,1-dicyano, tricyano-, and tricyanochloro-ethylene and the relative rates of formation of the two isotopically isomeric adducts were found by analysis of the product. Duplicate samples of each adduct were made in separate experiments, two with anthracene and two with 9-d-anthracene. The peaks in the PMR spectra from the bridge-head protons, H_a (lower field) and H_b (higher field), were scanned a minimum of 20 times each, using a digital voltmeter to measure the areas. As an indication of the experimental error, for the acrylonitrile adducts the ratio of the intensity of the absorption from the aromatic to that from the bridge-head protons was 8·01 for the deuteriated adduct and 4·02 for the undeuteriated. Table 2 summarizes the chemical shifts of the peaks in the spectra of the undeuteriated adducts and Table 3 gives the mean values of the ratio of H_a to H_b in the deuteriated and undeuteriated adducts. For the more symmetrical dienophiles, tricyanoethylene and tricyanovinyl chloride, the observed isotope effect is barely outside the experimental error, but the less symmetrical dienophiles, acrylonitrile and methylenemalononitrile

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* Measurement of the rate of reaction of 9-d-anthracene also might have been an alternative way of resolving the ambiguity.

[7] T. J. Katz and R. Dessau, *J. Amer. Chem. Soc.* **85**, 2172 (1963).

[8] S. Seltzer, *J. Amer. Chem. Soc.* **85**, 1360 (1963).

do show a definite isotope effect (about half that reported for addition of diphenylketene to cyclohexene[7]). That the isotope effect for acrylonitrile is, rather surprisingly, the same as for methylenemalononitrile accords with the fact that the effect for tricyanoethylene is hardly measurable. In each case the isotope effect indicates an unsymmetrical transition state with the more electrophilic end of the dienophile's double bond engaged in more advanced bond formation.*

In the dissociation of the *exo*-adduct of 2-methylfuran and d-maleic anhydride, where a mono-deuteriated, otherwise symmetrical dienophile and an unsymmetrical diene are involved, rather than *vice versa* as in our system, the two isotopic isomers react at the same speed.[8] Evidently the electronic difference between H and CN at the two ends of ethylene in our system is far greater than the trivial difference between H and CH_3 at the two ends of the very polarizable furan.

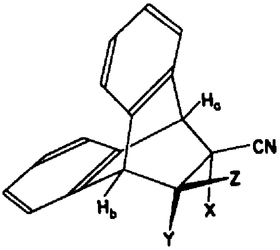

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Table 4 summarizes other measurements of deuterium isotope effects in the Diels-Alder reaction that appeared during and after our work. The anthracene–tetracyanoethylene reaction is the only case that has been examined in both directions (if in different solvents). As with the reaction of 9-d-anthracene with acrylonitrile and methylenemalononitrile, the electron affinity, in this range, appears not to change the isotope effect: k_D/k_H is the same for addition of 9,10-d_2-anthracene to maleic anhydride as to tetracyanoethylene. We agree (as already stated) that the value of 1·06 is consistent with a single symmetrical transition state, with both new bonds less than half formed, but we do not think Van Sickle and Rodin[9] are justified in citing their figures for k_H/k_D—valuable though they are—as evidence against a two-step mechanism: for all their compounds (Table 4) were symmetrically deuteriated, and, *per α-deuterium atom*, 1·06 on the one-step mechanism becomes 1·12 on the two-step mechanism (where only one (sp^2) C—H is rehybridizing in the transition state of the slow step), just the value expected. We hope our results on 9-d-anthracene have helped to discount the latter interpretation.

On the other hand, in the rather special case of the loss of carbon dioxide from the α-pyrone–maleic anhydride adduct the C^{13} and O^{18} primary isotope effects have been

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* The values of H_a/H_b in Table 3 give the relative rates of formation of the two deuterio-isomeric adducts: they are not kinetic isotope effects directly comparable to k_H/k_D given elsewhere in this paper, because the value for undeuteriated anthracene is not known (presumably an undetermined amount slower still).

[9] D. E. Van Sickle and J. O. Rodin, *J. Amer. Chem, Soc.* **86**, 3091 (1964).

Table 1. Addition of tetracyanoethylene to anthracene and 9,10-d_2-anthracene

Solvent	Dielectric const	Temp°C	k_H l. mole^{-1} sec.$^{-1}$	k_D l. mole^{-1} sec.$^{-1}$	k_H/k_D	Δ(ΔF) cal.mole^{-1}
benzene	2·28	30·0	0·466 ± 0·009	0·531 ± 0·013	0·88	−43
chlorobenzene	5·62	30·0	2·22 ± 0·07	2·47 ± 0·09	0·90	−36
cyclohexanone	18·3	20·0	1·54 ± 0·02	1·71 ± 0·04	0·90	−34
propionitrile	27·2	40·0	1·72 ± 0·05	1·94 ± 0·06	0·89	−41
acetonitrile	37·5	20·0	1·87 ± 0·08	2·00 ± 0·09	0·93	−23
propylene carbonate	61·7	40·0	2·84 ± 0·15	3·16 ± 0·14	0·90	−37
ethanol[a]	24·3	50·0	5·36 ± 0·14	4·58 ± 0·14	1·17	+56·5

[a] Dissociation of adduct.

Table 2. Chemical shifts in anthracene adducts(I) τ values

X	Y	Z	solvent	Ar	H_a	H_b
H	H	H	MeCN	2·75(m)	5·41(d)	5·62(t)
CN	H	H	Me_2CO	2·62(m)	4·76(s)	5·33(t)
CN	CN	H	MeCN	2·55(m)	4·71(s)	5·05(d)
CN	CN	Cl	Me_2CO	2·42(m)	4·29(s)	4·53(s)
CN	CN	CN	Me_2CO	2·40(m)	4·22(s)	

(s = singlet: d = doublet: t = triplet: m = multiplet)

Table 3. Mean isotope effects in addition to 9-d-anthracene

X	Y	Z	H_a/H_b anthracene	H_a/H_b 9-d-anthracene
H	H	H	1·00	1·07
CN	H	H	—	1·07
CN	CN	H	0·99	1·02
CN	CN	Cl	1·04	1·06

Table 4. Secondary deuterium isotope effects in the Diels-Alder reaction

Addition	Temp. °C.	k_D/k_H per D atom	Ref.
Deuteriated diene			
1. 9,10-d_2-anthracene + maleic anhydride	25	1·06	9
2. 9,10-d_2-anthracene + TCNE	25	1·06	—
3. 1,1,4,4-d_4-butadiene + maleic anhydride	25	1·07	9
Deuteriated dienophile			
4. anthracene + d_2-maleic anhydride	25	1·05	9
5. butadiene + d_2-maleic anhydride	25	1·01	9
6. cyclopentadiene + d_2-maleic anhydride (*endo*-adduct)	25	1·03	9
Dissociation			
Deuteriated diene			
7. 2-methyl-5-d-furan + maleic anhydride (*exo*-adduct)	50	1·08	10
8. 9,10-d_2-anthracene + TCNE	50	1·09	—
Deuteriated dienophile			
9. 2-methylfuran + d_2-maleic anhydride	50	1·08	10

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[10] S. Seltzer, *Tetrahedron Letters* 457 (1962).

interpreted[11] in terms of a transition state in which only the C—C bond is breaking. It seems reasonable that the Diels-Alder reactions of such an unsymmetrical dienophile (or dienophobe) as carbon dioxide should lie near the extreme end of the range of mechanisms with an unsymmetrical transition state.

EXPERIMENTAL

Preparation of 9, 10-d$_2$*anthracene*

Of the available methods, those of Petukhov[12] and Walker[13] were used, in preference to exchange with d-H_2SO_4 (which gives non-specifically deuteriated product) and the Grignard method,[14] which in our hands gave poor conversions. Improvement in the method of isolating 9, 10-d$_2$-anthracene from the reaction mixture, which contains some 9, 10-dibromoanthracene, was effected by adding TCNE to the filtered reaction mixture, and precipitating the anthracene–TCNE adduct. This intermediate can then readily be analysed for deuterium by quantitative NMR spectroscopy, and subsequently solvolysed in boiling 10% aqueous EtOH in excellent yield to 9,10-d$_2$-anthracene. Two recrystallizations from either dry benzene or EtOH gave 28% material, m.p. 219–220°. Purification of the adduct for kinetic purposes was realized by two recrystallizations from $CHCl_3$ or acetone–petrol, m.p. 267–270° (dec).

IR spectra. (a) 9,10-d$_2$-anthracene[15] (Nujol): 680 (m), 745 (m), 785 (s), 900 (m), 955 (m), 1610 (w), 2230 (w). (b) TCNE adduct (Nujol): 760–780 (s), 2300 (w), 3100 (w).

Deuterium analysis. Samples of 9,10-d$_2$-anthracene and the TCNE adduct were analysed by Dr. J. Nemeth using the falling drop method and found to contain 0·1800 and 0·1795 atom fraction deuterium respectively.

Preparation of 9-d-*anthracene*

The procedure employed was identical to that above, using 9-bromoanthracene as starting material. Overall yield of pure 9-d-anthracene was 32%, m.p. 218–219°.

IR spectrum (Nujol)[15]: 740–760 (s). 790 (m), 850 (m), 890 (m), 955 (m). 1610 (w), 2260 (w), 3050 (w).

Deuterium analysis. The NMR spectrum of the acrylonitrile–9-d-anthracene adduct in acetone was recorded, and the ratio of aromatic to bridgehead protons found to be 8·10, by digital voltmeter. This corresponds to 99% deuteriation at the 9-position, and although probably less accurate than combustion analysis, still indicates between 97–100% deuteriation.

Preparation and purification of dienophiles

(i) *acrylonitrile.* BDH reagent grade acrylonitrile was twice distilled (b.p. 746 mm 77°) under dry N_2, and used immediately. VPC analysis showed only one peak.

(ii) *methylenemalononitrile.* The method (A) of Ardis *et al.*[16] was used, from 1,1,3,3-tetracyanopropane, but gave only 10% product.

(iii) *tricyanoethylene.* The reaction sequence of Dickinson *et al.*[17] was followed successfully, starting from glycolonitrile.[18]

(iv) *tricyanovinyl chloride.* This material was prepared as recommended,[17] from tetramethylammonium tricyanoethenolate.[19]

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[12] G. G. Petukhov, N. V. Likhovidova and R. F. Galiulina, *Chem. Abstr.* **58**, 489 (1963).

[13] P. Walker, *J. Org. Chem.* **26**, 2994 (1961).

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[16] A. E. Ardis, S. J. Averill, H. Gilbert, F. F. Miller, R. F. Schmidt, F. D. Stewart and H. L. Trumbull. *J. Amer. Chem. Soc.* **72**, 1305 (1950).

[17] C. L. Dickinson, D. W. Wiley and B. C. McKusick, *J. Amer. Chem. Soc.* **82**, 6132 (1960).

[18] R. Gaudry, *Org. Synth.* **27**, 41 (1947).

[19] B. C. McKusick, R. E. Heckert, T. L. Cairns, D. D. Coffman and H. F. Mower, *J. Amer. Chem. Soc.* **80**, 2806 (1958).

Addition of dienophiles to anthracene and 9-d-anthracene

The relative rates of addition of the dienophiles to 9,10-dimethylanthracene are approximately as follows:[23] TCNE 10^{10}; tricyanoethylene 6 × 10^{8}; methylenemalonontrile 10^{5}; acrylonitrile 1 (at 20° in dioxan). Thus only addition of the last to 9-d-anthracene required heat, the others reacting rapidly at room temperature.

(i) Equimolar acrylonitrile and anthracene were dissolved in dry benzene together with a small quantity of hydroquinone,[20] and heated in a sealed tube for 16 hr at 160°. Chromatography of the residue, followed by recrystallization from EtOH, gave 77% of the known 1:1 adduct, m.p. 115–117°. (Found: C, 88·36; H, 5·69; N, 5·99. Calc. for $C_{17}H_{13}N$: C, 88·28; H, 5·67; N. 6·06.) Direct recrystallization of the reaction mixture from ether-petrol gave a 2:1 complex of the acrylonitrile–anthracene adduct and hydroquinone, m.p. 132–133°. (Found: C, 84·08; H, 5·52; O, 5·63; N, 4·77. $C_{40}H_{31}O_2N_2$ requires: C, 83·88; H, 5·65; O, 5·59; N, 4·89%.) The presence of 0·5 mole hydroquinone per mole was confirmed by comparitive NMR [absorptions at 3·22 (2-proton singlet) and 3·58τ (1-proton singlet)]. The ratio of hydroquinone is lower than that normally encountered in H-bonded clathrate complexes.[21]

(ii) *methylenemalononitrile*. Previously reported methods[22] afforded 70% of the 1:1 adduct, m.p. 187–190°, with 9-d-anthracene as diene.

(iii) *tricyanoethylene*. Application of published methods[17] converted the unstable dienophile into 86% of the 1:1 adduct, m.p. 228–230°, after two recrystallizations from benzene. (Found: C, 81·44; H, 3·99; N, 14·74. $C_{19}H_{11}N_3$ requires: C, 81·12; H, 3·94; N, 14·94%.)

(iv) *tricyanovinyl chloride*. By the same technique,[17] 75% of the 1:1 adduct was obtained, m.p. 210–15° (dec). (Found: C, 72·19; H, 3·23; N, 13·18; Cl, 11·32. $C_{19}H_{10}N_3Cl$ requires: C, 72·26; H, 3·20: N, 13·31; Cl, 11·23%.) All samples of the above adducts for quantitative NMR measurements were vacuum dried at 40° for 24 hr before use.

Acknowledgement—P. B. acknowledges with gratitude an Esso Research Studentship.

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[21] [a] H. M. Powell, *J. Chem. Soc.* 468 (1950); [b] D. E. Palin and H. M. Powell, *Ibid.* 208 (1947).

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