Acidity of Hydrocarbons. XXXIII. Kinetic Acidities of the Hydrogens in Triptycene toward Cesium Cyclohexylamide[1,2]

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Abstract: Bridgehead tritium exchange from triptycene with cesium cyclohexylamide in cyclohexylamine at 25° is 0.24 as fast as that of benzene. The primary isotope effect, $k_D/k_T = 2.2$, and the relative rates of *m*-methyl (0.51) and *p*-methyl (0.34) ring substituents indicate that the transition state for exchange has a substantially broken C–H bond and high carbanion character with essentially no internal return. The kinetic acidity of the bridgehead position is accounted for quantitatively by the electron-attracting polar effect of the aromatic carbons and by the s character of the C–H bond. Of the aryl hydrogens, the kinetic acidity of the 1-hydrogen is 7.3 times that of the 2-hydrogen; this difference is interpreted on the basis of increased p character of the bonding orbitals to the bridgehead carbons.

Caldwell[4] found that exchange of a bridgehead tritium from triptycene with cesium cyclohexylamide (CsCHA) in cyclohexylamine (CHA) is faster than exchange from cyclohexane by some eight powers of ten and is slower than benzene exchange by only a factor of 4. The intermediate triptycyl carbanion has considerable interest as a necessarily pyramidal ion that cannot conjugate with the benzene rings. In this paper we present the results of a more detailed study of this system including kinetics, isotope effects, and some substituent effects.

Experimental Section

Melting points are uncorrected. Radioactive counting was obtained with Nuclear Chicago Mark I[5] or Model 720 liquid scintillation counters. Ultraviolet spectra were obtained with Perkin-Elmer Model 202 or Cary Model 14 spectrophotometers. Benzene-*t* and toluene-2-*t* were prepared[6] by quenching the Grignard reagents with tritiated water.[7]

Anthracene-9-*t*. 9-Bromoanthracene (0.5 g, 0.002 mole) in ether and excess phenyllithium were allowed to react for 10 min at 0°. The reaction was quenched with 25 μl of tritiated water (1 Ci/g) and 1 g of untritiated anthracene was added. The ether layer was dried over $MgSO_4$ and was evaporated giving a solid which was chromatographed in benzene on acidic alumina. Recrystallization from ethanol gave 1 g of anthracene-9-*t*, mp 216–217°. This material had an activity of 1×10^8 dpm/mmole (theoretical, 140×10^8).

The use of deuterium oxide to which some tritiated water has been added gave anthracene-9-*d*(*t*).

Anthracene-2-*t*. The Grignard reagent prepared from 3 g of 2-chloroanthracene and 0.07 g of magnesium in THF was quenched with 1 μl of THO (1 Ci/g) followed by 1 ml of water. Ether was added, and the mixture was filtered, chromatographed, and recrystallized from alcohol giving 0.15 g of anthracene-2-*t*, mp 218–219°. This material was diluted with 3 g of anthracene to give product having 8.8×10^7 dpm/mmole (theoretical: 300×10^7 dpm/mmole). Anthracene-1-*t* was prepared earlier.[8]

2-Methylanthracene-9-*t*. *o*-(*p*-Methylbenzyl)benzoic acid (5 g, prepared[9] by hydrogenation over 10% Pd–C in alcohol and HCl of *o*-(*p*-methylbenzoyl)benzoic acid[10]), mp 134–135° (lit.[11] mp 133.5–134°), was shaken vigorously with 25 ml of concentrated sulfuric acid for 2 min at 0°. The yellow solution was poured into ice water and the solid was filtered, washed, and crystallized from acetone–water giving 1 g of 2-methylanthrone, mp 102-102° (lit.[12] mp 103°).

In a glove box under nitrogen atmosphere a solution of 0.5 g of 2-methylanthrone in THF was mixed with a small amount of a THF solution of lithium aluminum hydride followed by tritium-enriched $LiAlH_4$ and finally an excess of $LiAlH_4$. The first $LiAlH_4$ served to remove traces of moisture since only a minute quantity of tritium-enriched hydride was used. The product was chromatographed on alumina to give 41% of 2-methylanthracene-9-*t*, mp 209–210°.

2-Methylanthracene-10-*t*. After standing for 8 min, a solution of 1.5 g (6.6 mmole) of *o*-(*m*-methylbenzyl)benzoic acid (prepared[9] by hydrogenation over Pd–C and HCl in alcohol of *o*-(*m*-methylbenzoyl)benzoic acid[13]), mp 104.8–105° (lit.[14] mp 101–102°), in 25 ml of liquid HF was poured into ice water and extracted with ether. The ether solution was dried and evaporated and the solid was crystallized from acetone–water giving 50% of 3-methylanthrone, mp 96–97° (lit.[12] mp 103°), which was reduced as above to give 2-methylanthracene-10-*t*, mp 209–210°.

Triptycenes. Two general procedures were used. In the first, the method of Friedman and Logullo[15] was applied to the preparation of triptycene-9-*t* and -9-*d*(*t*). To a refluxing solution of 1.4 g (7.8 mmole) of anthracene-9-*d*(*t*) and 1.03 g (8.8 mmole) of isoamyl nitrite in 25 ml of methylene chloride was added a solution of 1.12 g (8.8 mmole) of anthranilic acid in 6 ml of acetone over a 3-hr period. The solvents were removed on a rotary evaporator and 10 ml of xylene and 0.60 g of N-ethylmaleimide were added. The solution was refluxed for 1 hr and cooled, and 35 ml of water and 50 ml of methylene chloride were added. The organic layer was washed with aqueous KOH and dried, and the solvents were removed under vacuum. The resulting solid was washed with cold methanol and cold ligroin, chromatographed in benzene on acidic alumina, and recrystallized from methylcyclohexane giving 0.63 g (31%) of triptycene-9-*d*(*t*), mp 255–256° (lit.[15] mp 253–254°), having activity of 19×10^6 dpm/mmole.

Friedman's[16] improved method was used with the remaining compounds with the following general procedure. A mixture of 8 ml of concentrated HCl and 20 ml of isoamyl nitrite was added to a

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[1] Paper XXXII: A. Streitwieser, Jr., and W. R. Young, *J. Amer. Chem. Soc.*, **91**, 529 (1969).

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[3] National Institutes of Health Predoctoral Fellow, 1964–1966.

[4] A. Streitwieser, Jr., R. A. Caldwell, and M. R. Granger, *J. Amer. Chem. Soc.*, **86**, 3578 (1964).

[5] This instrument was purchased with a grant from E. I. du Pont de Nemours and Co.

[6] Preparations by R. A. Caldwell.

[7] The use of tritiated water is no longer recommended in such preparations because of low radiochemical yields. Acetic acid-*t* as the quenching reagent generally gives much better results.

[8] A. Streitwieser, Jr., and R. G. Lawler, *J. Amer. Chem. Soc.*, **87**, 5388 (1965).

[9] Preparation by D. Holtz.

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[16] We are indebted to Professor L. Friedman for these directions in advance of publication.

Table I. Exchange Kinetics with Cesium Cyclohexylamide at 25°

Run no.	Hydrocarbon	[RH], mole/l.	[CsCHA],[a] mole/l.	k_T, 10^4 sec^{-1}	Relative rate k(toluene-2-t) = 1	Relative rate k(benzene-t) = 1
33[b]	Triptycene-9-*t*		0.011	1.56	1.22	0.24
	Toluene-2-*t*			1.28		
109	Triptycene-9-*t*	0.0028	0.012	3.25 ± 0.10	1.25 ± 0.05	0.25
	Toluene-2-*t*	0.065		2.59 ± 0.08		
363	Triptycene-9-*d,t*	0.0044	0.009	2.63 ± 0.30[c]	1.20 ± 0.25	0.24
	Toluene-2-*t*	0.065		2.20 ± 0.38		
237[d]	Triptycene-9-*t*	0.0028	0.043	38.6 ± 0.5	1.41 ± 0.13	
	Toluene-2-*t*	0.065		27.4 ± 2.1		
501	2-Methyltriptycene-9-*t*	0.0036	0.017	1.19	0.62	
	Toluene-2-*t*	0.14		1.92		
525	2-Methyltriptycene-10-*t*	0.0045	0.026	1.58	0.41	
	Toluene-2-*t*	0.14		3.89		
333	Triptycene-2-*t*	0.0030	0.018	21.7 ± 0.5		2.77 ± 0.17
	Benzene-*t*	0.083		7.83 ± 0.43		
339	Triptycene-1-*t*	0.0023	0.0011	69.0 ± 3		19 ± 1
	Benzene-*t*	0.083		3.6 ± 0.2		
351	Triptycene-1-*t*	0.0018		128 ± 4		21 ± 1
	Benzene-*t*	0.083		6.19 ± 0.10		
579	Triptycene-9-*d,t*	0.0028		3.0[e]		

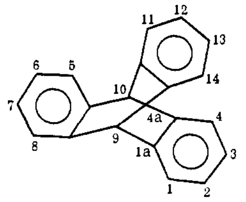
[a] Approximate base concentration. [b] Run by R. A. Caldwell. [c] $k_D = (7.37 \pm 0.85) \times 10^{-4}$ sec^{-1}; $k_D/k_T = 2.8 \pm 0.4$. [d] At 50.0°. [e] $k_D/k_T = 2.24$ by direct comparison of loss of D *vs.* loss of T.

stirred solution of 10.95 g of anthranilic acid in 120 ml of absolute alcohol at 0°. After stirring for 20 min, 120 ml of ether was added and stirring was continued for 5 min. The crystals were collected and washed with ether to give 85% of benzenediazonium-2-carboxylate hydrochloride. A mixture of 1 equiv of this product, 1 equiv of the anthracene, and 2 equiv of propylene oxide in 1,2-dichloroethane was refluxed for 2 hr. Diethyl Carbitol was added and the solvents were distilled until the head temperature reached 150°, whereupon N-ethylmaleimide was added and the mixture was refluxed for 25 min. The mixture was cooled, aqueous methanolic KOH was added, and the mixture was cooled to 0° and filtered or extracted with methylcyclohexane. The product was purified by chromatography in benzene on acidic alumina and recrystallized from methylcyclohexane. In this way we prepared triptycene-1-*t*, mp 256–257°, triptycene-2-*t*, mp 255–257°, 2-methyltriptycene-9-*t*, mp 161–164° (lit.[15] mp 173.5–174°), and 2-methyltriptycene-10-*t*, mp 164–166°.

Kinetics. The kinetic studies were carried out as described previously[17] with one modification. After extracting the kinetic points into a suitable hydrocarbon solvent, the compounds were best separated by vacuum transfer rather than by direct proportional flow counting techniques. In the present study each kinetic run contained a nonvolatile triptycene derivative and a volatile standard hydrocarbon, either toluene-2-*t* or benzene-*t*. Each aliquot was placed in a flask on one side of an inverted U tube which was attached to the vacuum line. After degassing, the volatiles were transferred to a flask on the other side of the U tube leaving the nonvolatile compound behind. A sample was counted by standard methods. The volatile solution was assayed by uv spectrometry and also counted. Deuterium content was followed by low-voltage mass spectrometry. The kinetic results were analyzed by Perrin's program[18] to obtain the correct least-squares rate constants with the approximate standard deviations. The results of the kinetic runs are summarized in Table I.

Results and Discussion

The present results on the rate of tritium exchange between cesium cyclohexylamide (CsCHA) and triptycene-9-*t* relative to toluene-2-*t* agree completely with the earlier result of Caldwell.[4] As usual with these exchange kinetics the difficulty in assaying the CsCHA concentration renders the second-order rate constants approximate and difficult to reproduce; consequently, in our runs a standard compound is always present so that relative rates are determined directly. Such relative rates are generally reproducible to a few per cent.



triptycene

In order to evaluate whether this relative exchange rate has meaning as a measure of acidity in this novel case of a bridgehead triptycene position, we need first to study the structure of the transition state using typical physical organic chemical tools. We note first that runs 33, 109, and 363 in Table I show that the rate relative to the 2 position of toluene is essentially constant over about a twofold change in rate; hence, the kinetic order in base for triptycene is the same as that of an aryl hydrogen. The exchange of benzene has been shown previously to be of first order in CsCHA.[17]

From the results at 50 and 25°, triptycene-9-*t* compared to toluene-2-*t* has 1.1 kcal/mole higher activation energy and 4 eu higher entropy of activation. These numbers are relatively small and by themselves would suggest reasonably similar transition states for the two reactions.

Run 579 was conducted with deuterated and tritiated triptycene and the loss of both isotopes was followed carefully to give $k_D/k_T = 2.24$. As we have discussed previously,[17,19,20] this is a rather high value indicative of a simple proton transfer with substantial C–H bond breaking at the transition state. Moreover, we have used such high isotope effects as a routine criterion[17,18,20–24] for the absence of a significant internal return.[25]

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(18) A. Streitwieser, Jr., R. G. Lawler, and C. Perrin, *ibid.*, **87**, 5383 (1965).

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To evaluate the electronic nature of the transition state, we looked at a *m*- and *p*-methyl substituent. The rate effects of these groups relative to the parent molecule are similar to that of the substituted toluenes wih LiCHA as shown in Table II. According to the unconjugated *m*-methyl group, the transition state for triptycene with CsCHA has more carbanion character than does that for the benzylic position of toluene toward LiCHA. However, the opposite trend is shown by the *p*-methyl effect taken at face value. But here we must recognize that the carbanion center in the triptycene case cannot conjugate in a direct sense; hence, we would not expect the effective electron-donating power of the *p*-methyl group to be as marked in the triptycyl anion case as with benzyl anion. Nevertheless, the greater rate-retarding effect of the more distant *p*-methyl compared to *m*-methyl demonstrates that some conjugation is operative whether it be a π-inductive conjugation of charge to the *para* position or direct electron donation from the *p*-methyl group to the carbon adjacent to the reacting bridgehead. In any event, the comparable magnitude of the methyl effects in the two systems does demonstrate that the amount of carbanion character in the triptycene transition state is comparable to that in the toluene case; in the latter case, a relatively large value for ρ, 4.0, has already been demonstrated.[21]

Table II. Effect of Methyl Substituents

Substituent	9-Triptycene CsCHA, 25°	α-Toluene LiCHA, 50° [a]
H	1.00	1.00
m-Me	0.51	0.60
p-Me	0.34	0.31

[a] Reference 21.

The results of this study are that the triptycene exchange is quite comparable to the other systems we have studied, that the reaction is a simple proton transfer in which the C–H bond is extensively broken at the transition state, and that the reacting carbon has substantial negative charge. These are the necessary criteria for use of such rates as measures of acidity; hence, it is clear that the bridgehead position has comparable acidity to that of benzene and has much greater acidity than cyclohexane.[4,24] This result contrasts with that of Bartlett and Lewis,[26] who were not able to metalate 9-bromotriptycene directly. Their results can probably be interpreted with radical reactions since Wittig and Schöllkopf[27] have shown that this bromide will undergo halogen–metal exchange with butyllithium in ether. Moreover, these authors emphasize that the 9-triptycyllithium is colorless, indicating the lack of conjugation.

The kinetic acidity of triptycene is thus consistent with the chemistry of corresponding organometallic derivatives and appears to be a realistic measure of thermodynamic acidity in solution. The enhancement of acidity over that of alkanes is undoubtedly due, at least in part, to the electron-attracting polar effect of the benzene rings; however, another significant factor is increased s character in the bridgehead C–H bond.

The crystal structure of 9-bromotriptycene has been determined by Palmer and Templeton.[28] They find the C–C_9–C and C–C_{10}–C bond angles to be 107.5 and 107.4°, respectively. These less-than-tetrahedral angles imply greater p character in these bonds, hence, greater s character in the bond to the bridgehead hydrogen. For bond orbitals taken to be colinear with the bond axis, an angle of 107.5° corresponds to sp$^{3.32}$ hybridization of the three equivalent orbitals from the bridgehead carbon and leaves an sp$^{2.26}$ hybrid orbital for the bond to hydrogen.

The C^{13}–H coupling constant for triptycene of 145 ± 1 cps[29] gives an alternative value of the hybridization, sp$^{2.45}$. Although both methods give a result of greater s character than sp^3, the two results do not agree at all well. It seems quite likely that the coupling constant result is more nearly correct and that the value derived from the bond angles is in error because the bonds are partially bent; that is, it seems reasonable that the assumption that the bond orbitals are colinear with the bond axis is in error for the bridgehead bonds.

Our studies of tritium exchange of cycloalkanes with CsCHA led to a correlation between such exchange rates and J(C^{13}–H).[30] This correlation applied to J(C^{13}–H) for triptycene yields a rate factor of 2.80 ± 0.16 powers of ten compared to cyclohexane. Triptycene is 7.34 log units more reactive than cyclohexane; hence, 4.5 ± 0.2 log units are presumably to be attributed to inductive effects.

One approach to an independent evaluation of polar effects in triptycene comes from the correlation established earlier between the kinetic acidities of aryl hydrogens toward LiCHA and a field effect function defined as $\Sigma_j 1/r_{ij}$ in which r_{ij} is the distance between the aromatic carbon at which reaction is occurring and each other aromatic carbon j in the polycyclic aromatic.[8,31] In the triptycyl anion, the lone pair is also in the nodal plane of each of the aromatic rings and the same correlation can be applied in a straightforward way. It should be noted that the $\Sigma 1/r$ correlation predicts a reactivity for an isolated C_{sp^2}–H much the same as that given by the J(C^{13}–H) correlation with cycloalkanes.[30] Bond distances and angles for triptycene were estimated from Palmer's structure of 9-bromotriptycene to give $\Sigma 1/r = 6.66$ Å^{-1}, corresponding to a polar effect log relative rate of 4.15 ± 0.34.[32] This value compares

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(30) A. Streitwieser, Jr., R. A. Caldwell, and W. R. Young, *J. Amer. Chem. Soc.*, **91**, 529 (1969). The correlation in this paper applies to J(C^{13}–H) values derived from proton nmr spectra. J. J. Burke and P. C. Lauterbur [*J. Amer. Chem. Soc.*, **86**, 1870 (1964)] have shown that significantly different values are derived from the C^{13} nmr spectra of cycloalkanes because of asymmetry of the observed absorptions. Although none of our conclusions is altered by these small variations, due caution must be used in applying the correlations. We are indebted to Professor Lauterbur for valuable correspondence on this point.

(31) Our most recent least-squares treatment gives the correlation for polycyclic hydrocarbons in terms of rates relative to benzene as $\log k/k_0 = 0.624\Sigma 1/r - 1.609$, with a standard deviation of the slope of 0.051.

(32) We are indebted to M. Maskornick for this calculation.

excellently with the polar effect log relative rate of 4.5 ± 0.2 derived above. No better agreement is to be expected since the lone pair of triptycyl anion has different hybridization from that of a phenyl anion, the r_{ij} values are distances between carbon nuclei rather than to the center of charge density in the lone pair, and we have taken cyclohexane as an assumed standard with no inductive effect component. The comparison of a tertiary hydrogen of triptycene with a secondary hydrogen of cyclohexane involves an error of unknown magnitude, pending the results of further studies in progress. Nevertheless, the success of the $\Sigma 1/r$ correlation is remarkable and leaves no doubt that the approximate magnitude of the polar effect contribution of the aromatic carbons in triptycene has been correctly estimated. This success carries the corollary that the exchange reactions of the polycyclic aromatics, triptycene, and cycloalkanes all have comparable Brønsted coefficients. Thus, of the total rate enhancement of triptycene over a corresponding alkane, roughly one-third is associated with the greater than tetrahedral s character of the bridgehead C–H and two-thirds is associated with the inductive effect of the aromatic rings. This necessitates a small change in our earlier estimate of the inductive effect contribution to the enhanced acidity of triphenylmethane over an alkane analog.[4] Of the 10^{13} higher reactivity of triphenylmethane compared to cyclohexane, about one-third on a log scale is to be attributed to inductive effects.

Aryl Hydrogens. Both aryl hydrogens in triptycene are more reactive than a benzene hydrogen and the 1 position is 7.3 times as reactive toward CsCHA as the 2-hydrogen (Table I). It is difficult to estimate an expected reactivity for these positions. The bridgehead carbons can be regarded as alkyl substituents which would be expected to be rate retarding (the *o*-, *m*-, and *p*-toluene ring positions are, respectively, 0.20, 0.59, and 0.52 as reactive as benzene[22]) but the other two benzene rings are expected to be rate enhancing. The blend of these two contrasting influences is expected to be different for the two positions. The alkyl effect is expected to reduce the reactivity of the 1 position (*ortho* and *meta* to bridgehead carbons) significantly compared to the 2 position (*meta* and *para* to bridgehead carbons). The other benzene rings are expected to enhance the reactivity of the 1 position compared to the 2, but not by a large factor—note that the 1 position of naphthalene is only 1.6 times as reactive as the 2 position toward LiCHA.[18] The observed rate factor of 7.3 in triptycene appears to be much too large to account for on these bases but is consistent with the "strained-ring effect" proposed recently.[33] In 9-bromotriptycene, Palmer and Templeton[28] found the C_9–C_{1a}–C_{4a} and C_{10}–C_{4a}–C_{1a} bond angles to be 110.7 and 112.2°, respectively. These angles are less than the normal 120° and are expected to involve orbitals from the benzene carbons that are higher in p character than sp^2; hence, the C_{1a} orbital in the C_{1a}–C_1 bond is expected to be higher in s character than sp^2. Since C_1 is thus bonded to an orbital of greater electronegativity than in a standard aromatic ring, the C_1–H bond is expected to have enhanced acidity, as is found experimentally. Note that this interpretation of a strain effect differs from another theory which has been applied recently to some electrophilic aromatic substitutions.[34] The latter interpretation is based on a change in bond order between ground state and transition state and does not apply to the present acidity case.

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