HYDROGEN TRANSFER FROM ALCOHOL DONORS TO AROMATIC SUBSTRATES

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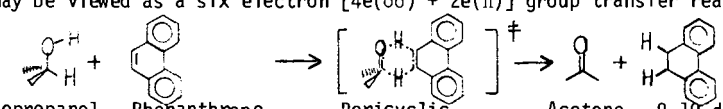
Introduction:

The use of alcohols in coal liquefaction by donor solvents dates to the earliest works (1) wherein the tetralin donor used also contained phenol and cresol additives; chemically similar mixtures have been used more recently (2,3) to simulate commercial donor solvents. Alcohols have also directly been employed as hydrogen donors for coal liquefaction, in which application isopropanol, cyclohexanol and o-cyclohexylphenol have proven effective (4), whereas t-butanol is ineffective (5). The mechanism of hydrogen transfer from alcohol donors to coal is obscure. However, free radical types of mechanisms, such as recently proposed (6,7) for coal liquefaction, seem especially unsatisfactory because the essential step would have to involve abstraction of a relatively strongly bonded hydrogen in the alcohol by a coal fragment radical formed from homolysis of a weak bond in the coal.

The present work was motivated by a hypothesis (8,9) that coal liquefaction may entail concerted, pericyclic reaction paths. In this context, hydrogen transfer from an alcohol donor, such as isopropanol, to a coal acceptor, such as phenanthrene, may be viewed as a six electron [4e(σσ) + 2e(Π)] group transfer reaction:

(RO)



Isopropanol 4e(σσ) Donor — Phenanthrene 2e(Π) Acceptor — Pericyclic Transition State — Acetone — 9,10 dihydrophenanthrene

According to the Woodward-Hoffmann (10) rules for orbital symmetry conservation, reaction (RO) would be thermally allowed for supra-supra stereochemistry, which is sterically favorable.

Pursuit of our hydrogen transfer hypothesis suggested exploration of a grid comprising two alcohol donors, namely cyclohexanol and ortho-cyclohexylphenol, and two aromatic acceptors, namely phenanthrene and anthracene. Of these substrates, the cyclohexanol is a 4e(σσ) donor akin to isopropanol while the o-cyclohexylphenol is a 6e(σΠσ) donor of the contrary orbital symmetry. Similarly, the phenanthrene, a 2e(Π) acceptor, has orbital symmetry opposite to anthracene which is a 4e(ΠΠ) acceptor. In the 2 x 2 matrix of thermal reactions between these donor-acceptor pairs, combinations with a total of (4n+2)e should theoretically (10) be allowed in supra-supra stereochemistry while those with a total of (4n)e should be forbidden in supra-supra but allowed in supra-antara stereochemistry. Such differences should be manifest, and hence experimentally discernible, in the respective reaction kinetics. Figure 1 illustrates these principles of orbital symmetry conservation for the present hydrogen transfer reactions. Experimental results obtained to date with the cyclohexanol donor are reported in this paper.

Experimental:

All experiments were conducted in stainless steel batch reactors with an

internal volume of 0.503 cm^3; the reactors were immersed in a salt bath for times ranging from 0.16 to 12 hours at temperatures from 300 to 425°C. Heating and cooling times were calculated to be insignificant compared with reaction times. Experiments conducted in an argon atmosphere, when compared with reactions in air, indicated no effect of atmosphere on reaction rate. Vapor-liquid equilibrium calculations were used to ensure that >95% of the reactants remained in the liquid phase at all times. Upon reaction and subsequent quenching, the products were dissolved in solvent--toluene for anthracene reactions, carbon tetrachloride for phenanthrene reactions--and analyzed on an HP 5720 gas chromatograph. Product identification was based on G.C. coinjection techniques as well as nmr spectra. Material balance closure was effected in all experiments, and particular care was taken to effect a hydrogen transfer balance. Thus, we define a ratio H of the mols of hydrogen donated, h_d, as measured by appearance of dehydrogenated donor, to the mols of hydrogen accepted, h_a, as measured by the appearance of hydrogenated acceptor; in all cases $H = (h_d/h_a) = 1.00 \pm 0.08$. The chemicals used were all of purity > 99.5% as received; the anthracene and phenanthrene substrates were further purified and assayed to ensure that the content of the related dihydro compound was below detection limits, i.e., < 0.05%.

Results.

Preliminary investigation of reaction pathways revealed that three types of reactions occurred. First, the hydrogen transfer reaction, our primary objective, which is symbolically represented by:

(R1) $D + A \rightarrow DD + HA$

D, A, DD, and HA are respectively the donor, acceptor, dehydrogenated donor and hydrogenated acceptor; the initial (donor/acceptor) ratio is termed S. Second, the hydrogenated acceptor HA could, in general, revert to the original acceptor:

(R2) $HA \rightarrow A$

This usually occurred by elimination of molecular hydrogen but disproprotionation, with formation of a further hydrogenated form of HA, was also possible. Third, the donor D could react by paths other than (1), typically suffering pyrolytic decomposition:

(R3) $D \rightarrow$ products

In the present work, D = cyclohexanol (CHL), A = either anthracene (ANT) or phenanthrene (PHE), DD = cyclohexanone (CHN), and HA = either dihydroanthracene (DHA) or dihydrophenanthrene (DHP). The experimental grid constructed to examine the preceding pathways is shown in Table 1, which indicates substrate(s), diluent, and reaction conditions of temperature, time and concentration for each of five sets of reactions.

Broadly, the experimental results showed that hydrogen transfer, (R1), was by far the major reaction in all circumstances. Reversion of hydrogenated acceptor, (R2), was usually small relative to (R1) but occurred to an appreciable extent at the higher temperatures and holding times. Donor decomposition, (R3), was always negligible relative to (R1) at $T \leqslant 400$ C. Thus, in deriving the desired kinetic parameters for (R1), the experimental data could directly be treated as if (R1) were the only reaction occurring; corrections for (R2), which were small, allowed more refined parameters to be obtained for (R1) while corrections for (R3) were so small as to be neglible. The kinetic analyses employed are summarized in Table 2.

Data for hydrogen transfer from cyclohexanol to anthracene at T = 375 C are presented in Figure 2, which essentially displays anthracene conversion x vs time for various initial donor/acceptor ratios, $15.4 > S > 0.25$. The ordinate of Figure 2 is a function of conversion chosen to test the presumed second order form of (R1), as suggested by Case 1 of Table 2. Following a typical set of data, say S = 15.4 (squares), the ordinate, starting from the origin, increases with increasing time, linearly at low times, $t < 2$ hr, but with decreasing slope thereafter, eventually becoming constant, independent of time, for $t > 6$ hr. Physically, the initial linear portion represents the kinetics of the forward reaction (R1) alone, while the long-time asymptote of constant conversion represents an approach to equilbrium. It is noteworthy that the initial slopes are much the same for all S, directly yielding $k_1 = 5.6 \times 10^{-6}$ l/mol s independent of substrate proportions, which supports the second order kinetics presumed for (R1). It is also interesting that the asymptotic long-time conversions available at each of S = 1 and S = 15.4 both lead to apparent equilibrium constants $K_{app} = [X^2/(1-X)(S-X)] \sim 0.02$.

Refined rate constants, derived from the initial slope data of Figure 2 after taking account of all other reactions, are displayed in Figure 3 on co-ordinates of $\log_{10}k_1$ vs $\log_{10}S$. It can be seen that $\log_{10}k_1 = -5.25 \pm 0.07$ over $-0.6 < \log_{10}S < 1.2$, i.e. a variation in $\log_{10}k$ of about 0.1 unit over 1.8 decades of substrate proportions ranging on either side of stochiometric. The observed invariance of k relative to S confirms that the cyclohexanol-anthracene hydrogen transfer reaction follows second order kinetics at T = 375 C.

Having established the order, and hence being assured of a meaningful bimolecular rate constant k_1, the hydrogen transfer reaction kinetics were explored over the temperature range from 300-400 C at a fixed S = 4. An Arrhenius plot of these results is presented in Figure 4, using coordinates of $\log_{10}k_1$ vs θ^{-1}, where $\theta^{-1} = (10^3/4.573\ T$ in Kelvins) is an inverse temperature scale; it should be noted that an Arrhenius relation of form $\log_{10}k = \log_{10}A - E^*/\theta$, where A is the pre-exponential factor with units of k and E* is the activation energy in kcal/mol, will yield a straight line on Figure 4 with slope $\Delta\log_{10}k/\Delta\theta^{-1} = -E^*$. Data for the cyclohexanol-anthracene reaction (circles in Figure 4) show $\log_{10}k_1$ linearly related to θ^{-1} over nearly two decades of the ordinate. The best fit then yielded the hitherto unknown Arrhenius parameters, $\log_{10}A$(ℓ/mol s) = 6.0 ± 0.2 and E* (kcal/mol) = 33.1 ± 0.6, which were our goal.

Hydrogen transfer from cyclohexanol to phenanthrene, set 2 in Table 1, was investigated in a manner exactly analogous to that described for cyclohexanol-anthracene in Figures 2, 3, and 4, and similar conclusions could be drawn. Thus, for cyclohexanol-phenanthrene, at T = 400 C, plots akin to the earlier Figure 2 for initial donor/acceptor ratios $8 > S > 0.125$ yielded initial slopes independent of S, with $k_1 \sim 0.65 \times 10^{-6}$ ℓ/mol s. Also, asymptotic long-time conversions led to $k_{app} \sim 0.15 \times 10^{-3}$ at each of S = 4, 1, and 0.125. A further plot of $\log_{10}k_1$ vs $\log_{10}$ S, shown in Figure 3, yielded $\log_{10}k_1 = -6.2 \pm 0.2$ over the range $-0.9 < \log_{10}S < 0.9$, affirming the relative invariance of k to substrate proportions and showing the hydrogen-transfer kinetics to be second order. Finally, cyclohexanol-phenanthrene hydrogen transfer rate constants were derived at temperatures from 375-425 C at fixed S = 4. These results, plotted in Figure 4 (squares), yield Arrhenius parameters $\log_{10}A$(ℓ/mol S) = 7.6 ± 0.6 and E* (kcal/mol) = 42.5 ± 3.5. Since the data for cyclohexanol-phenanthrene span only a single decade of $\log_{10}k_1$, the corresponding Arrhenius parameters are subject to rather more uncertainty than in the case of cyclohexanol-anthracene.

Reversion of the hydrogenated acceptor to the original acceptor, general reaction (R2), was studied at the conditions indicated for entries 3 and 4 in Table 1, using dihydroanthracene (DHA) and dihydrophenanthrene (DHP) substrates with decalin

diluent, which latter was inert. In general, reversion occurred by two parallel pathways, namely hydrogen elimination (R2') and disproportionation (R2"), of the form:

$$\text{(R2')} \quad HA \xrightarrow{k_2'} A + H_2$$

$$\text{(R2")} \quad 2HA \xrightarrow{k_2''} A + JA$$

where all symbols have their earlier meaning and JA is a more hydrogenated form of the acceptor, e.g. tetrahydroanthracene.

Experiments with DHA substrate at T = 375 C revealed that with neat substrate, 4.0 M, the initial rates of (R2') and (R2") were of comparable magnitudes. With increasing dilution, however, the initial rates of (R2") decreased relative to (R2') until, at the lowest substrate concentration of 0.2 M, (R2") was negligible relative to (R2'). Further, examination of the kinetics showed (R2') to be strictly first order in DHA with $k_2' = (27 \pm 2) \times 10^{-6}\ s^{-1}$ at initial substrate concentrations from 0.23 to 4.3 mol/liter; reaction (R2") was approximately second order at initial concentrations from 0.9 to 4.3 mol/liter, where it could be measured, yielding $k_2'' = (37 \pm 11) \times 10^{-6}$ ℓ/mol s. Additional experiments with neat DHA over the temperature range 325-400 C provided Arrhenius parameters $\log_{10}A(s^{-1}) = 12.5 \pm 0.6$ and E* (kcal/mol) = 50.8 ± 0.8 for the first order DHA reversion rate constant k_2'; these experiments also yielded data for (R2") but corresponding Arrhenius parameters are yet unavailable, pending confirmation of the reaction order.

Experiments with DHP substrate showed (R2') to be the only reversion pathway, with (R2") undetectable. At T = 425 C, the reaction was strictly first order with $k_2' = (34 \pm 2) \times 10^{-6}\ s^{-1}$ at initial substrate concentrations from 0.22 to 4.0 mol/liter. Arrhenius parameters for DHP reversion over the temperature range 375-420 C were $\log_{10}A(s^{-1}) = 12.6 \pm 0.3$ and E* (kcal/mol) = 58.1 ± 0.8.

Relating the reversion experiments (R2) to the hydrogen transfer experiments (R1), it should be noted that in the latter reaction, the hydrogenated acceptor initially appears at infinite dilution. Thus, of the two reversion pathways, (R2') and (R2"), which are respectively first and second order, (R2') makes much the more significant contribution. Analytically, the overall reversion rate constant $k_2 = k_2' + k_2''[HA] \rightarrow k_2'$ as $[HA] \rightarrow 0$. The cyclohexanol-anthracene series of experiments further confirmed this inference in that the tetrahydroanthracene product symptomatic of (R2") was not detected at times < 2 hr. The rate data obtained for (R2') thus adequately accounted for the reversion reaction (R2) in the present study.

Finally, in regard to the donor decomposition reaction (R3), set 5 in Table 1, the cyclohexanol alone was substantially stable at T ≤ 400 C, with fractional decompositions < 0.03 in 4 hr. At T = 425 C cyclohexanol decomposition, initially to cyclohexanone, became appreciable, with a pseudo first order rate constant $k_3 \sim 20 \times 10^{-6}\ s^{-1}$. In processing the hydrogen transfer data, corrections for (R3) were always negligible.

Discussion:

Kinetic data for hydrogen transfer reactions between alcohol donors and aromatic acceptors have not hitherto been reported, precluding comparisons with earlier work. However, the experimental evidence can reasonably be interpreted in favor of a concerted reaction mechanism. Both the hydrogen transfer reactions studied exhibited second order kinetics, being first order in each of the donor and acceptor. This is a necessary condition that must be fulfilled for (R2) to be considered

bimolecular, as written. Further, the Arrhenius parameters ($\log_{10}A$(ℓ/mol s), E*(kcal/mol)) were respectively for CHL-ANT (6.0, 33.1) and for CHL-PHE (7.6, 42.5). Of these the $\log_{10}A \sim 6.8 \pm 0.8$ represent activation entropies ΔS^{+} (cal/mol K) = -31.7 ± 3.7 which are large and negative and of much the same magnitude reported (11,12) for Diels-Alder reaction which is well known to be a concerted cyclo-addition (10). There is evidently close steric similarity between the pericyclic transition state of our hydrogen transfer reaction, as shown in the prototype (RO), and the transition state for cyclo-addition. The observed activation energies E*(kcal/mol) = 38 ± 5 cannot independently be interpreted, though their magnitudes are entirely comparable to values known for allowed hydrogen shifts (13), which involve similar orbital interactions.

While the thermochemistry of the present hydrogen transfer reactions is not well known, estimates (14) suggest (ΔS^{o}_{r}(cal/molK), ΔH^{o}_{r}(kcal/mol) for CHL-ANT (~ 0, ~ 0) and for CHL-PHE (~ 0, +5); i.e. the reactions are virtually thermoneutral. Consequently, invoking microscopic reversibility, Arrhenius parameters for the reverse hydrogen transfer reactions should be quite similar to those obtained for the forward reactions. In regard to thermochemistry it is also worth noting that the present experiments led to apparent equilibrium constructs of order 10^{-2} for CHL-ANT and 0.15×10^{-3} for CHL-PHE at T = 400 C. These cannot be directly interpreted for want of activity coefficient data but their ratio should depend solely on the differences between the entropies and enthalpies of hydrogenation of the acceptors. Estimates (14) of ($\Delta H^{o}_{f}, S^{o}$) for each of ANT, DHA, PHE, DHP lead, at T = 400 C, to the theoretical ratio K(CHL-ANT)/K(CHL-PHE) ~ 60 which is of the order of the experimentally observed ratio K_{app}(CHL-ANT/K_{app}(CHL-PHE) ~ 70.

It is interesting to compare the present hydrogen transfer from cyclohexanol with that from Δ^{1}-dialin, a hydrocarbon donor of the same orbital symmetry. Comparable experiments reported elsewhere (15) yielded ($\log_{10}A$(ℓ/mol s), E*(kcal/mol)) = (6.1, 31.0) for the Δ^{1}-dialin-phenanthrene system; $\log_{10}A$ is similar to that obtained in the present work for CHL-PHE while the activation energy is lower by an amount comparable to the reduction in the enthalpy of reaction, in rough agreement with the Evans-Polanyi principle.

The reversion reactions (R2) also merit brief discussion inasmuch as kinetic data have not hitherto been reported for hydrogen elimination from either of the DHA or DHP substrates studied in this work. The general reaction (R2') has literature precedent, the case HA = 1,4 cyclohexadiene, A = benzene having been studied (13,16) in the gas phase and found to be unimolecular with Arrhenius parameters ($\log_{10}A$ (s^{-1}), E*(kcal/mol)) = (12.4, 43.8); the reaction mechanism has been interpreted (10) as a concerted thermally-allowed 6e suprafacial group transfer. In the present study, (R2') with HA = DHA was strictly unimolecular with Arrhenius parameters ($\log_{10}A$,E*) = (12.6, 50.8). Since there is a clear stereo-electronic analogy between hydrogen elimination from 1,4 cyclohexadiene and that from 9,10-dihydroanthracene, the analogous kinetic data can be taken to imply that the latter reaction is also a 6e pericyclic group transfer. The case of (R2') with HA = DHP which is unimolecular with ($\log_{10}A$,E*) = (12.6, 58.1) is not yet directly amenable to theoretical interpretation. According to the Woodward-Hoffman rules (10), this hydrogen elimination is thermally allowed with antara-supra stereochemistry and without further stereochemical information it is not obvious whether the higher E* relative to DHA represents a stereochemical demand or an orbital symmetry barrier. However, it is interesting that in regard to hydrogen elimination, DHP is more refractory than DHA to essentially the same extent that 1,3 cyclohexadiene (17) is more refractory than 1,4 cyclohexadiene (16).

Finally it is worth noting that with present system of donors and acceptors,

the hydrogen transfer from donor to acceptor was appreciably faster than either hydrogenated acceptor reversion or donor decomposition. This is evidently desirable in the context of actual coal liquefaction operations. Further studies, with appropriate coal-related model donors and acceptors, which thus elucidate the pathways for hydrogen transfer could be practially useful in suggesting donors and processing conditions for the optimal deployment of hydrogen during direct liquefaction.

Conclusions:

1. Hydrogen transfer reactions between cyclohexanol (CHL) donor and each of anthracene (ANT) and phenanthrene (PHE) acceptors have been studied in the liquid phase at temperatures from 300 to 425 C, times from 0.16 to 12.0 hr and initial donor/acceptor ratios of 0.125 to 15.4.

2. In addition to the desired hydrogen transfer reaction (R1), two other pathways were observed, namely, (R2) reversion of the hydrogenated acceptor to original acceptor by way of both hydrogen elimination (R2') and disproportionation (R2"); and (R3) pyrolytic donor decomposition. The kinetics of (R2) and (R3) were also investigated and it was found that (R2) was small and (R3) negligible relative to (R1).

3. The hydrogen transfer reactions were bimolecular, being of order one in each of donor and acceptor. Arrhenius parameters ($\log_{10}A$(ℓ/mol s), E*(kcal/mol)) were respectively for CHL-ANT (6.0 ± 0.2, 33.1 ± 0.6) and for CHL-PHE (7.6 ± 0.6, 42.5 ± 3.5).

4. The observed molecularity and Arrhenius parameters suggest a concerted pericyclic mechanism for the hydrogen transfer with a relatively tight transition state akin to that well known for Diels-Alder cycloaddition.

5. Hydrogen elimination from dihydroanthracene (DHA) and dihydrophenthrene (DHP) liquids was studied at temperatures from 300 to 450 C, times from 0.16 to 10.0 hrs and substrate concentration ranges of 0.2 to 4.0 mol/liter.

6. The hydrogen elimination reactions were strictly unimolecular. Arrhenius parameters ($\log_{10}A(s^{-1})$, E*(kcal/mol) were respectively for DHA (12.6 ± 0.6, 50.8 ± 0.8) and for DHP (12.6 ± 0.3, 58.1 ± 0.8).

7. The observed hydrogen elimination from DHA to ANT is strikingly analogous to thatfrom 1,4 cyclohexadiene to benzene and suggests a similar concerted pericyclic group transfer reaction.

Acknowledgement:

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Table 1. Reaction Conditions.

Set	Substrates	Diluent	Reaction Conditions: Temperature C	Time hr	Concentration S or M
1	CHL + ANT	None	300-400	0.16-12.	0.25-16.
2	CHL + PHE	None	350-425	0.25-10.	0.25-8.0
3	DHA	DEC	300-400	0.16-10.	0.25-4.0(Neat)
4	DHP	DEC	375-450	0.25-12.	0.25-4.0(Neat)
5	CHL	None	325-425	0.25-10.0	4.0 ± 0.2

Notes: Compound abbreviations are as follows:
CHL - cyclohexanol ANT - anthracene PHE - phenanthrene
DEC - decalin DHA - 9,10 dihydroanthracene DHP - 9,10 dihydrophenanthrene

S = initial substrate ratio CHL/ANT or CHL/PHE (sets 1 and 2).
M = concentration, mol/liter of DHA, DHP or CHL (sets 3, 4, and 5).

Table 2. Kinetic Analyses

Reactions:

$$\text{(R1)} \quad D + A \xrightarrow{k_1} DD + HA$$
$$\text{(R2)} \quad HA \xrightarrow{k_2} A + H_2$$

Differential Equation: $d(HA)/dt = k_1(D)(A) - k_2(HA)$

Constraints:

$t = 0$: $(D/A)_0 = S$; $(HA/A)_0 = 0$
$t > 0$: $A_0 = A + HA$

Solutions:

Case 1. $k_2 = 0$, all S.

$$\frac{1}{A_0(S-1)} \ln\left[\frac{1 - (X/S)}{1 - X}\right] = k_1 t \quad ; \quad X = 1 - (A/A_0) = (HA/A_0)$$

Case 2. $k_2 > 0$, $S > 1$

$$\frac{1}{A_0 S(1+k_2/k_1 SA_0)} \ln\left[\frac{1}{(1-X(1+k_2/k_1 SA_0)}\right] = k_1 t$$

Case 3. $k_2 > 0$, $S < 1$

$$\ln\left[\frac{k_1 SA_0 \exp(-k_1 A_0 t)}{k_1 SA_0 \exp(-k_1 A_0 t) - k_2 X}\right] = k_2 t$$

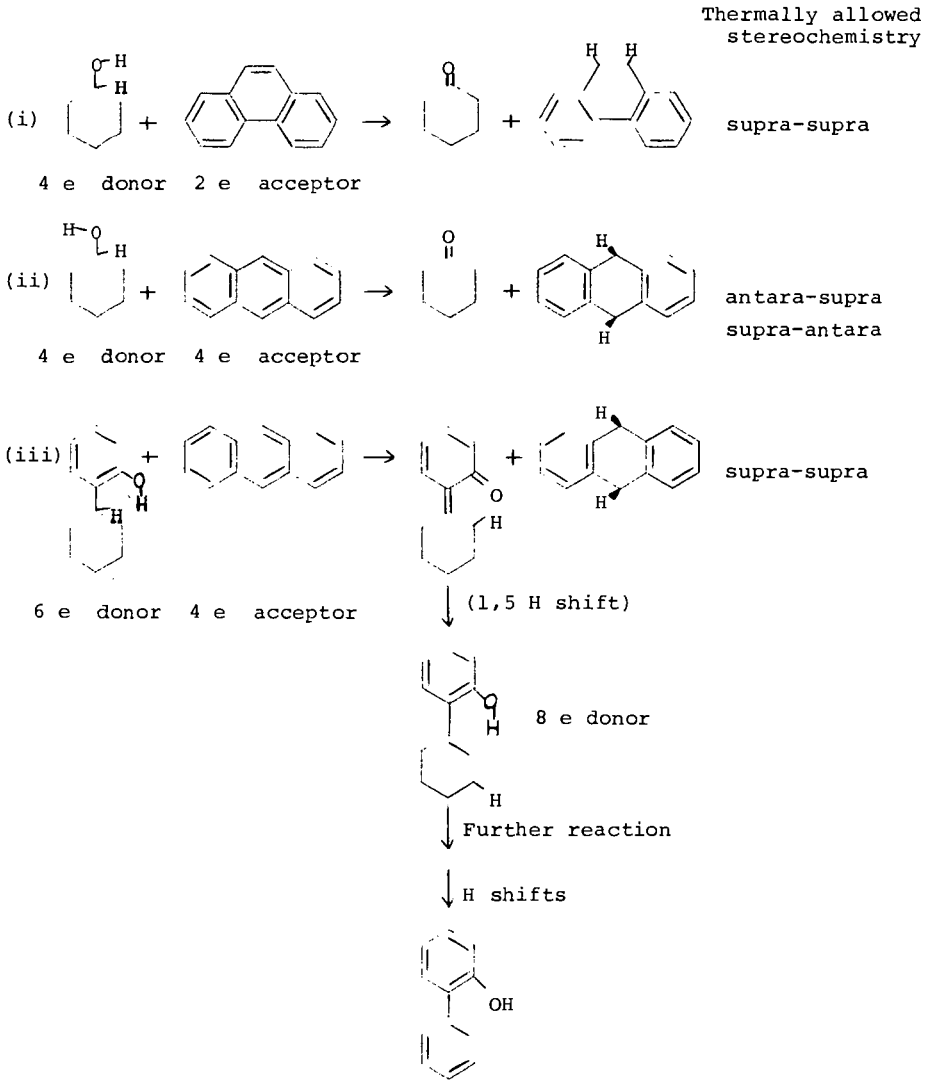


Figure 1. Orbital symmetry conservation in hydrogen transfer.

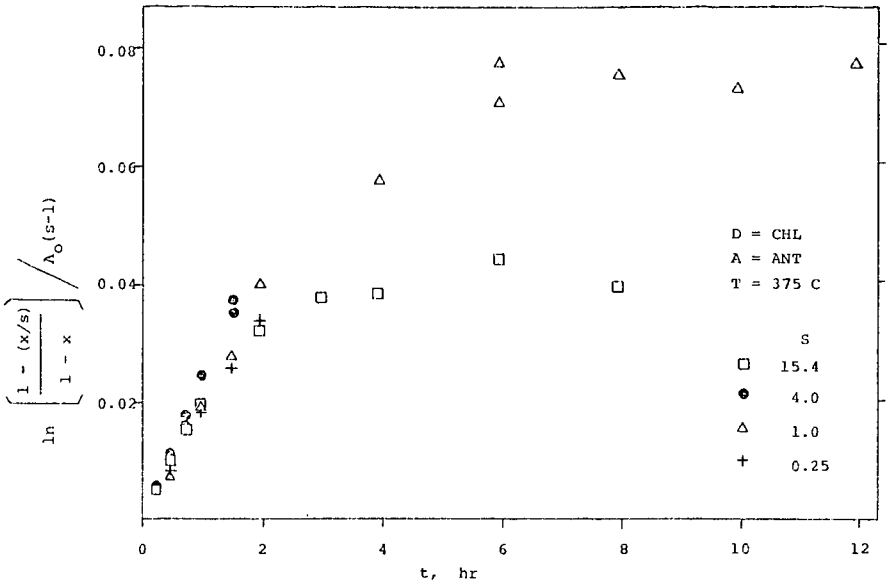


Figure 2. Hydrogen transfer kinetics: Conversion versus time.

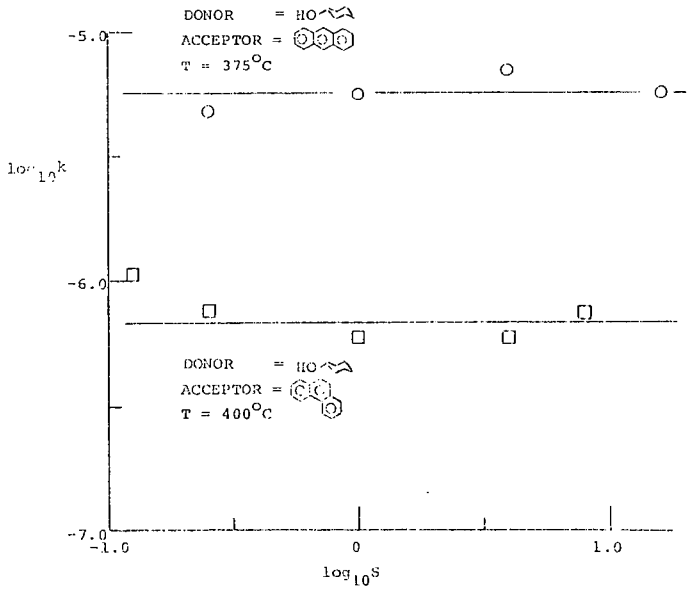
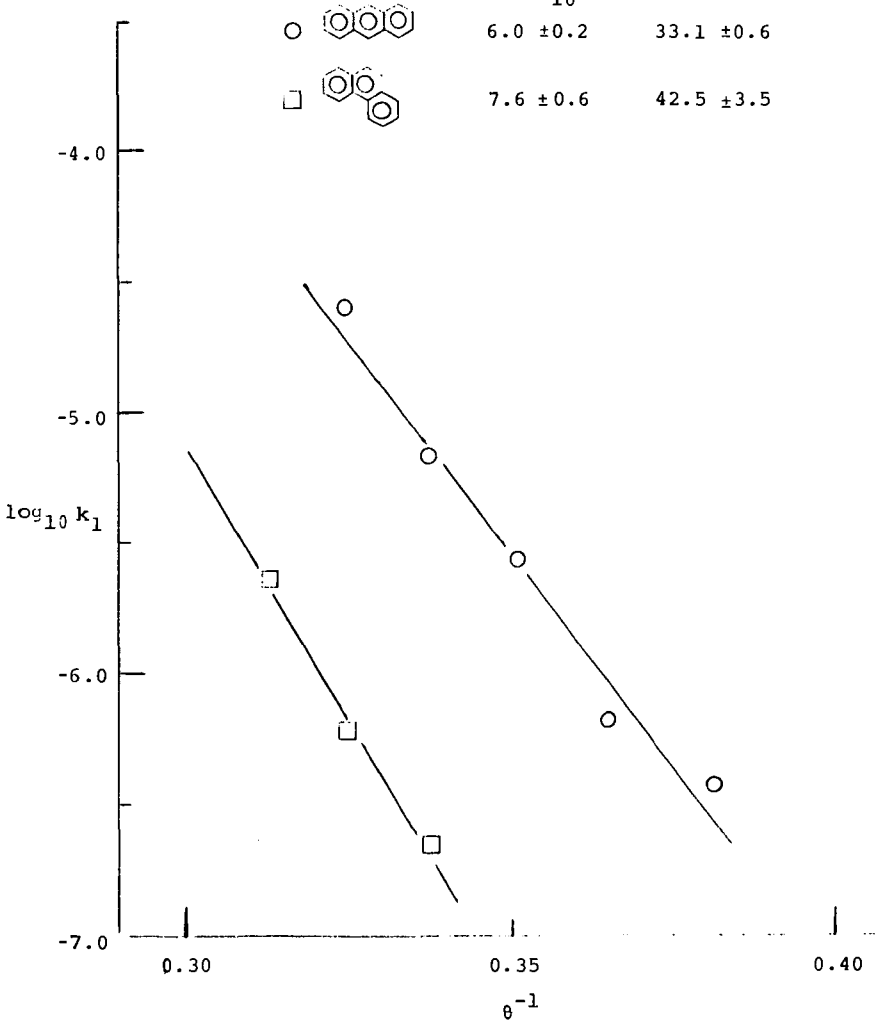


Figure 3. Hydrogen transfer kinetics:
Effect of (Donor/Acceptor) ratio.

Figure 4. Hydrogen transfer kinetics: Arrhenius plot.

REACTION: D + A → DD + HA

DONOR = HO-

ACCEPTOR	$\log_{10}A$	E^*
○	6.0 ±0.2	33.1 ±0.6
□	7.6 ±0.6	42.5 ±3.5