

Hydrogen Transfer Between 9,10-Positions in Anthracene and Phenanthrene

R. L. Billmers, L. L. Griffith, S. E. Stein

Chemical Kinetics Division
National Bureau of Standards
Gaithersburg, MD 20899

Introduction

The transfer of hydrogen between polyaromatic structures is an essential part of any realistic model of coal conversion chemistry. Not only do these processes affect the distribution of available hydrogen, but they are also intimately involved in certain C-C and C-O bond-breaking and bond-forming processes and may even control free-radical concentrations [1].

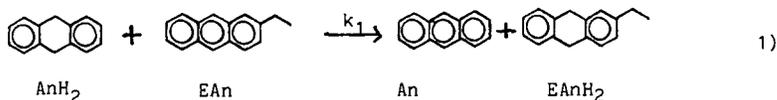
Chemical mechanisms responsible for these processes are not known. Currently, not only is there debate over the relative significance of individual reaction steps, but there are questions concerning the fundamental nature of these reactions, specifically, do they proceed by concerted, by free radical, or even by ionic steps.

Largely because of their intermediacy in reactions of tetralin, H-transfer reactions involving 1,2- and 1,4-dihydronaphthalene have been widely studied [2-5]. However, competitive addition and isomerization paths are open to these species, resulting in rather complex reaction mechanisms.

As a possibly simpler model system, we have chosen to study the transfer of hydrogen to the 9,10-positions of anthracene from 9,10-dihydrophenanthrene and from other 9,10-dihydroanthracene molecules. The particular stability of 9,10-dihydro structures as well as the absence of alternative pathways results in simpler mechanisms. Moreover, these three-ring structures themselves are of direct interest in coal chemistry. Experiments were done in sealed, evacuated pyrex tubes using conventional techniques [6].

9,10-Dihydroanthracene/2-Ethylanthracene Studies

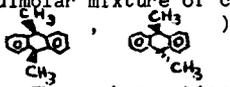
The kinetics of H-transfer from one anthracene structure to another was examined using the 2-ethyl group as a label,



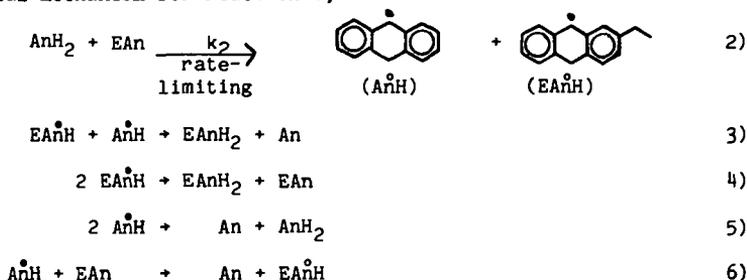
Rates followed the simple second-order expression (Figure 1),

$$\frac{d[\text{EAnH}_2]}{dt} = 10^{9.64 \pm 0.12} \exp\{-36,800 \pm 400 \text{ cal/RT}\} [\text{AnH}_2][\text{EAn}]$$

over the range $0.1 \lesssim [\text{AnH}_2]/[\text{EAn}] \lesssim 10$, and from undiluted AnH_2/EAn mixtures to mixtures diluted up to a factor of 100 in biphenyl. Rates were unaffected by heavy doses of radical initiators (1,1',2,2'-tetraphenylethane and 9,9'-bifluorene).

Addition of sufficiently large amounts of An to AnH_2/EAn mixtures caused a lowering of the rate of EAnH_2 formation (Figure 2). Using 9,10-dimethylantracene (, DMAn) in place of EAn led to a nearly equimolar mixture of cis- and trans- 9,10-dimethyl-9,10-dihydroanthracene ()

These observations are consistent with the following non-chain, free radical mechanism for reaction 1,



where step 6 is effective only when $[\text{AnH}_2]/[\text{EAn}] \lesssim 0.1$. Under most conditions, the observed rate is one-half the rate of reaction 2.

We rule out the importance of concerted reactions for the following reasons. (1) Concerted H_2 -transfer to DMAn would have formed only the cis isomer, but the product was 40-50% trans; (2) H-transfer to DMAn by $\text{HMn}(\text{CO})_5$ [7], which could not have occurred by conventional concerted processes, also led to nearly equimolar quantities of the cis- and trans-isomers; (3) equilibrium studies [8] have shown the cis-isomer to be slightly more stable from the trans-isomer; (4) separate studies showed that the cis-isomer did not isomerize to the trans-isomer under our conditions; (5) the slowing of the rate for EAnH_2 formation with added An cannot be explained by a concerted process.

In further support of our mechanism, the measured activation energy, along with the literature heat of the reaction $\text{AnH}_2 + \text{An} + \text{H}_2$ [9], yields a bond strength of $78.4 \pm 1.4 \text{ kcal mol}^{-1}$ for the AnH-H bond, in good agreement with a recently published value [10].

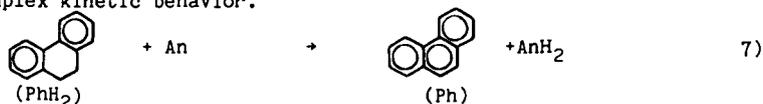
From the decline in rate with added An, we derive an approximate rate constant for k_6 of $110 \text{ M}^{-1}\text{s}^{-1}$ at 250°C . Assuming an A-Factor of $10^{8.5} \text{ M}^{-1}\text{s}^{-1}$, this reaction has an activation energy of $18.4 \text{ kcal mol}^{-1}$, in

agreement with the general conclusion of McMillen and co-workers [11] that such reactions (β -H-atom transfer) occur at rates comparable to those of conventional H-atom metathesis ($A\cdot + BH \rightarrow AH + B\cdot$).

The key result of our experiments is that molecular disproportionation, a step often proposed as a radical initiation step, is the critical step in H-transfer between 9,10-anthracene positions. Our results also provide indirect evidence for the occurrence of a β -H-transfer step, a potentially very significant step in hydrogen transfer mechanisms, but one which has only rarely been supported by kinetic evidence. More direct information on this reaction type was obtained in the following studies.

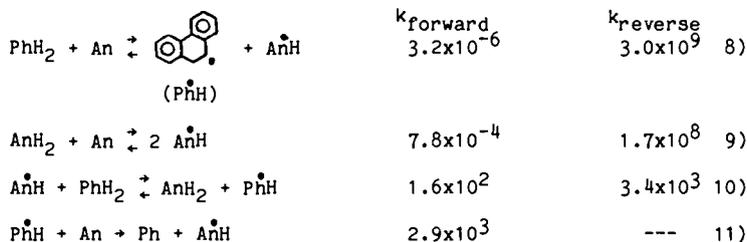
9,10-Dihydrophenanthrene/Anthracene Studies

Reaction 7 was studied at 350°C and was found to exhibit highly complex kinetic behavior.



The primary source of this complexity was the involvement of the product AnH_2 in the reaction (Figure 3). AnH_2 sharply catalyzed the reaction at low concentrations and moderately inhibited it at high concentrations.

A detailed computer model of this reaction was developed based on available and estimated rate and thermodynamic data. This model, given below, fits our results quite well (Figures 3-5).



This model contains two initiation steps (reactions 8 and 9). The predominant one depends on relative concentrations of PhH_2 and AnH_2 (they are equally effective at $[\text{AnH}_2] \sim 0.004 [\text{PhH}_2]$). The free radical chain described by reactions 10 and 11 was essential for modeling results. A sensitivity analysis of this model is in progress, and these rate constant values are therefore preliminary.

The question of whether H-transfer from PhH to An , step 11, proceeded through a direct, single step (β -H-transfer) or through a free H-atom intermediate ($\text{PhH} \rightarrow \text{Ph} + \text{H}$; $\text{H} + \text{An} \rightarrow \text{AnH}$), was answered in favor of the direct process on the basis of results of biphenyl dilution studies of $\text{PhH}_2/\text{An}/\text{AnH}_2$ mixtures (Figure 5).

A number of interesting features emerge from this mechanism. (1) The catalytic effect of AnH_2 is a result of its facility for forming radicals through molecular disproportionation (reaction 9). This step is virtually the same as the rate limiting step in the AnH_2/EAn mechanism (reaction 2). (2) In the absence of sufficient AnH_2 , PhH_2 donation to An served as the major radical initiation step. Since the PhH-H bond is considerably greater than the AnH-H bond [1], this initiation step is far slower than the AnH_2/An initiation step. (3) In this reaction, the $\beta\text{-H}$ -transfer step (reaction 11) is considerably more rapid than the corresponding step in the EAn/AnH_2 mechanism (reaction 6). Using an A-factor of $10^{8.5} \text{ M}^{-1} \text{ s}^{-1}$, the activation energy for reaction 11 is $14.4 \text{ kcal mol}^{-1}$, 4 kcal mol^{-1} lower than for reaction 6. This difference is probably due to the exothermicity of reaction 11 ($14 \pm 4 \text{ kcal mol}^{-1}$ [1,12]) compared to the thermoneutral nature of reaction 6. (4) The primary "reason" for the complex, chain reaction in the PhH_2/An mechanism appears to be to the high PhH-H bond strength compared to the AnH-H bond. This effectively shifts the former reaction to higher temperatures where chain reactions can occur. The above-mentioned facility of reaction 11 compared to reaction 6 also enhances chain reaction rates.

Conclusions

These studies indicate that H-transfer reactions among polyaromatic species proceed by free radical processes. Molecular disproportionation is the primary source of free radicals, and $\beta\text{-H}$ -transfer is a critical propagation step in chain reactions. Rates derived in these studies for both of these elementary processes provide a basis for estimating rates for related reactions. Mechanisms in the EAn/AnH_2 and An/PhH_2 reactions contain similar reaction steps, but follow entirely different kinetic laws.

In coal-related systems, An/AnH_2 structures can provide an efficient, steady supply of free radicals. The low bond strength of AnH-H is responsible for its special effectiveness as an H-donor in both radical-forming and radical-transfer steps [13]. The relatively high strength of the An-H bond allows the AnH radical to serve as an effective radical sink.

In a sense the Ph/PhH_2 system is opposite that of the An/AnH_2 system. The first bond (PhH-H) is significantly stronger and the second bond (Ph-H) weaker than corresponding bonds in AnH_2 . Therefore, PhH_2 is not nearly as effective as a free radical trap or initiator as is AnH_2 . On the other hand, PhH_2 can effectively hydrogenate molecules by $\beta\text{-H}$ -atom transfer to them through the labile PhH radical.

From a thermodynamic standpoint, PhH_2 is a more powerful hydrogenation agent than AnH_2 , and can irreversibly hydrogenate a wider range of structures [14]. However, AnH_2 is less prone to irreversible loss than PhH_2 and is therefore more likely to play a continuing role in hydrogen transfer mechanisms after PhH_2 structures have been destroyed.

Acknowledgement

This work was supported by a grant from the Gas Research Institute, Chicago, Illinois.

REFERENCES

1. Stein, S. E. in "New Approaches in Coal Chemistry", ACS Symp. Ser. 1981, **169**, Amer. Chem. Soc: Washington, D.C., p. 97.
2. Virk, P.S.; Bass, D. S.; Eppig, C. P.; Ekpanyong, D. J. Am. Chem. Soc. Div. Fuel Preprints 1979, **24**, (2), 144.
3. King, H. H.; Stock, L. M. Fuel 1981, **60**, 748.
4. Allen, D. T.; Gavalas, G. R. Int. J. Chem. Kinetics 1983, **15**, 219
5. Franz, J. A.; Camaioni, D. M.; Beishline, R. R.; Dalling, D. K. J. Org. Chem. 1984, **49**, 3563.
6. Stein, S. E.; Robaugh, D. A.; Alfieri, A. D.; Miller, R. E. J. Am. Chem. Soc. 1982, **104**, 6567.
7. Sweanyu, R; Butler, S. C.; Halpern, J. J. Organometallic Chem. 1981, **213**, 487.
8. Harvey, R. B; Arzadon, L.; Grant, J.; Urberg, K. J. Amer. Chem. Soc. 1969, **91**, 4535.
- 9a. Cox, J. D.; Pilcher, G. "Thermochemistry of Organic and Organometallic Compounds" 1970, Academic Press: New York
- 9b. Shaw, R.; Golden, D. M.; Benson, S. W. J. Phys. Chem. 1977, **81**, 1716.
10. McMillen, D. F.; Golden, D. M. Ann. Rev. Phys. Chem. 1982, **33**, 493.
11. McMillen, D. F.; Ogier, W. C.; Chang, S. J.; Fleming, R. H.; Malhotra, R. Proceedings Int. Conf. Coal Sci. 1983, Pittsburgh, PA, p. 199
12. Stein, S. E. in "Coal Conversion Chemistry", R. Schollosberg, ed., Pergamon Press, in press.
13. Poutsma, M. L. in "Free Radicals", Vol. II., Kochi, J. ed.; Wiley: New York, 1973, p. 113.
14. Kline, E. A.; Harrison, M. E.; Farnum, B. W. Am. Chem. Soc. Fuel Chem. Div. Preprints 1982, **27**(3), 18; 1983, **28**(5), 155.

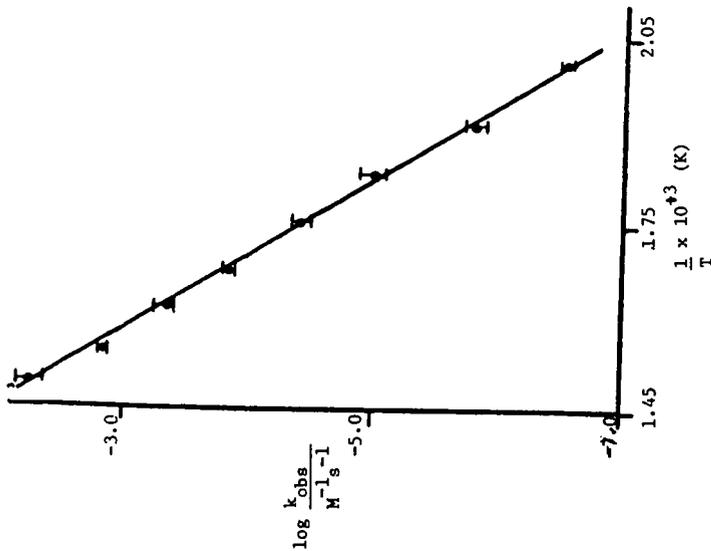


FIGURE 1. Arrhenius Plot for the Reaction $\text{EAn} + \text{AnH}_2 + \text{E/AnH}_2 + \text{An}$ (Reaction 2) Based on values obtained for $0.1 \leq [\text{AnH}_2]/[\text{EAn}] \leq 5.0$

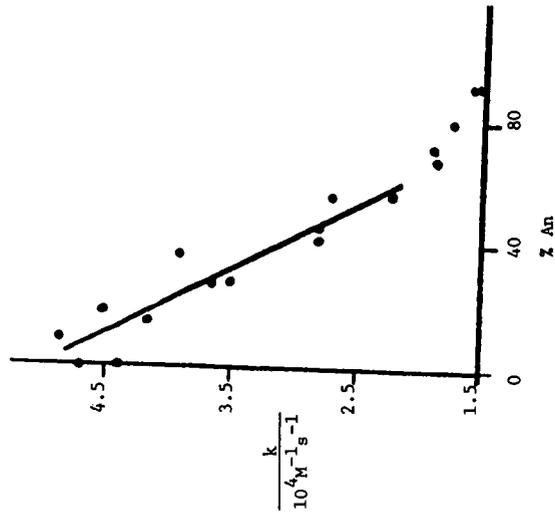


FIGURE 2. Effect of Added Anthracene on Reaction 2. $[\text{AnH}_2]/[\text{EAn}]$ $\sim 0.2\text{M}$; biphenyl was used as diluent; 350 C, 15 min.

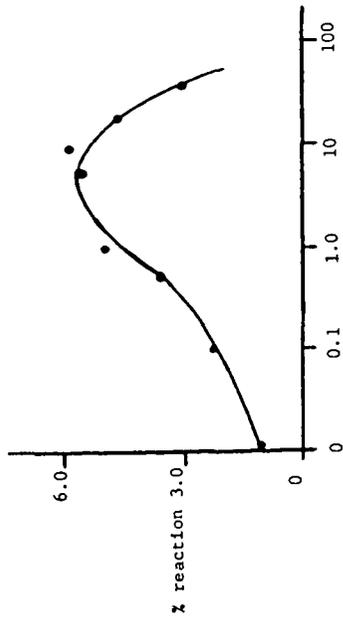


FIGURE 3. Effect of added AnH_2 on the Rate of the Reaction $\text{PhH}_2 + \text{An} \rightarrow \text{Ph} + \text{AnH}_2$. $T = 350$ C, times ~ 5 min, $[\text{PhH}_2]/[\text{An}] \sim 0.05$. Results of our kinetic model are shown by the solid line.

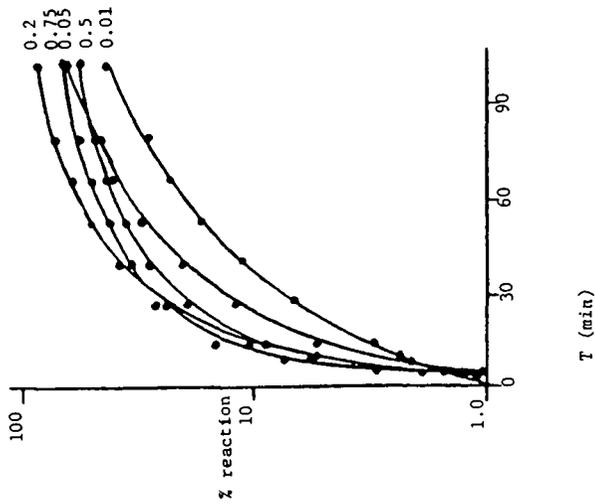


FIGURE 4. Percent Reaction for $\text{PhH}_2 + \text{An} \rightarrow \text{Ph} + \text{AnH}_2$ at 350 C. Numbers at end of curves are initial $[\text{PhH}_2]/[\text{An}]$ ratios. Points are experimental data - the line is from the kinetic model (see text).

FIGURE 5. Effect of Dilution by Biphenyl on the Rate of
 $\text{PhH}_2 + \text{An} \rightarrow \text{Ph} + \text{AnH}_2$. $T = 350^\circ\text{C}$, 30 min.
 $[\text{PhH}_2], [\text{AnH}_2]$.. Computer model is the solid line,
 broken line is for model containing the sequence
 $\text{PhH} \rightarrow \text{Ph} + \text{H}$, $\text{H} + \text{An} \rightarrow \text{HAn}$ in place of the direct
 reaction ($\text{PhH} + \text{An} \rightarrow \text{Ph} + \text{AnH}$)

