placed on the magnitude of ΔE_{corr} with the limited amount presently known about the wave functions of these large systems.

Limitations and Extensions. The methods given here are applicable to closed shell or single determinantal states. This includes the ground states of most molecules. The extension of these methods to nonclosed shell states is being studied. This will allow the treatment of potential energy surfaces as well as of electronic spectra.

For larger molecules, the approximations involved in the "pair populations" method need further basic study. The application of this method is limited by the need for simple MO wave functions and atomic pair correlation energies. The accuracy of pair correlation energies may improve. It is encouraging that ΔE_{corr} may be obtained quite easily from simple MO wave functions. This, of course, increases the applications of H.F. calculations. The agreement with available H.F. results is good, and calculations on larger systems would help test both these correlation methods and various ways of calculating approximate H.F. MO's.

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Pyrolysis of Deuterated Benzene

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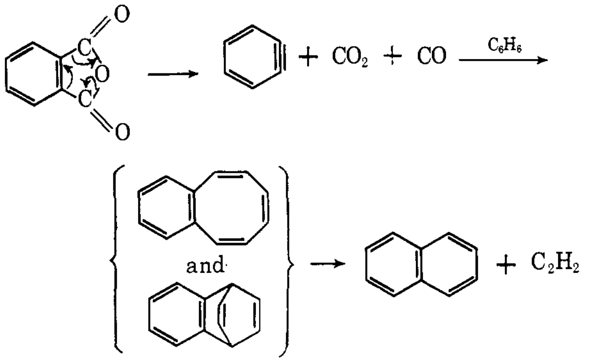
Abstract: Pyrolysis of benzene-d_1 and analysis of the pyrolysate revealed a considerable amount of scrambling of protium and deuterium in the recovered benzene. The isotopic composition of the biphenyl produced corresponded closely to that of the benzene that had undergone exchange. The data are best explained by formation of an intermediate phenylcyclohexadiene.

Benzyne, generated by pyrolysis of phthalic anhydride in benzene at 690°, reacts with the benzene to give mainly naphthalene and biphenyl.[2a] To elucidate the mechanism, we pyrolyzed a solution of phthalic anhydride in benzene-d_1. Naphthalene probably forms by 1,2- and 1,4-addition of benzyne to benzene, followed by elimination of acetylene.[2b]



(1)

Barring an appreciable isotope effect, two-thirds of the naphthalene should contain a deuterium atom and one-third only protium. Biphenyl arises in two ways: insertion of benzyne into a C–H bond of benzene and pyrolysis of benzene. Biphenyl from benzyne insertion should form with retention of the deuterium atom; biphenyl from benzene pyrolysis should—again ignoring any isotope effect—be d_0, d_1, and d_2 on the statistical basis of losing two, one, or zero deuterium atoms from a total of twelve protiums and deuteriums in the over-all reaction of two benzene molecules. The amount of biphenyl-d_1 in excess of an appropriately calculated value would presumably be due to the benzyne insertion reaction. Actual results are shown in Table I.

Table I. Products from Pyrolysis of Phthalic Anhydride in Benzene-d_1

Mass	No. of D atoms	Rel. abundance Calcd.[a]	Rel. abundance Found
		Naphthalene	
128	0	37.0	38.6
129	1	63.0	49.9
130	2	0	10.0
131	3	0	1.5
		Biphenyl	
154	0	...	8.2
155	1	...	35.4
156	2	...	44.8
157	3	...	8.8
158	4	...	0.9
159	5	...	0.1

[a] On the basis of 94.5% benzene-d_1 and 5.5% benzene-d_0 used as starting material.

The observed naphthalene results do not agree well with those calculated. Further, a considerable amount

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(1) (a) Amoco Chemicals Corp.; (b) American Oil Company.

(2) (a) E. K. Fields and S. Meyerson, *Chem. Commun.* (London), 474 (1965). The low-temperature reaction of benzyne from *o*-benzenediazoniumcarboxylate with benzene is discussed by R. G. Miller and M. Stiles, *J. Am. Chem. Soc.*, **85**, 1798 (1963); (b) R. F. C. Brown and R. K. Solly, *Chem. Ind.* (London), 181 (1965).

of both naphthalene and biphenyl contains more deuterium than could arise by the simple postulated reactions. To help clarify these results, benzene-d_1 was pyrolyzed alone at 690°, and both the benzene recovered and the biphenyl produced were analyzed for deuterium content. The results, shown in Table II, reveal a considerable amount of scrambling of deuterium and protium in the recovered benzene and explain the discrepancies between calculated and observed results in Table I. Oddly enough, although the pyrolysis of benzene to biphenyl and hydrogen was first recorded in 1866 by Berthelot[3] and has been investigated innumerable times since then, labeled benzene has never been pyrolyzed to find if the recovered benzene had the same isotopic composition as the original.

Table II. Products from Pyrolysis of Benzene-d_1[a]

No. of D atoms	Rel. abundance			
	4.2-Sec. contact		21-Sec. contact	
	Benzene	Biphenyl	Benzene	Biphenyl
0	10.5	7	27.4	13.7
1	84.5	31	52.6	35.0
2	4.9	53	17.3	33.8
3	0.1	9	2.5	13.8
4	...	...	0.2	3.2
5	...	...	...	0.5

[a] 94.5%-d_1, 5.5%-d_0.

Calculating the biphenyl composition from benzene of the initial and final isotopic compositions, on the assumption of random combination of two benzene molecules with random loss of two out of twelve hydrogen atoms and no isotope effect,[4] gave the figures in Table III. These comparisons strongly suggest that the biphenyl is formed preferentially from benzene that has undergone exchange. The agreement between calculated and observed isotopic distributions of the biphenyl at a contact time of 21 sec. is especially striking. The data may mean simply that the biphenyl undergoes exchange at the same rate as the benzene. However, the remarkably close agreement between calculated and observed distributions makes an explanation based on fortuitous considerations seem unlikely, and suggests instead a more fundamental cause.

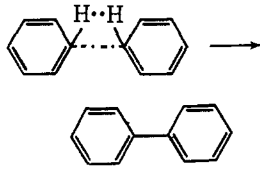
Table III. Calculated and Observed Isotopic Composition of Biphenyl

No. of D atoms	Rel. abundance					
	4.2-Sec. contact			21-Sec. contact		
	Calcd. from			Calcd. from		
	Initial	Final	Obsd.	Initial	Final	Obsd.
0	3.4	5.2	7	3.4	12.9	13.7
1	35.6	37.1	31	35.6	36.1	35.0
2	61.0	52.9	53	61.0	33.8	33.8
3	...	4.6	9	...	13.7	13.8
4	...	0.2	...	...	3.1	3.2
5	...	...	...	...	0.4	0.5

Specifically, the data suggest that hydrogen exchange among benzene molecules is much faster than biphenyl formation, and that the process by which benzene molecules undergo exchange leaves them in an activated state for the reaction to form biphenyl.

The deuterium statistics do not uniquely define a single reaction mechanism. In fact, the calculated distributions in Table III are nearly identical with distributions calculated on the assumption of random combination of two benzene molecules with random loss of one hydrogen atom from each of the reacting molecules.

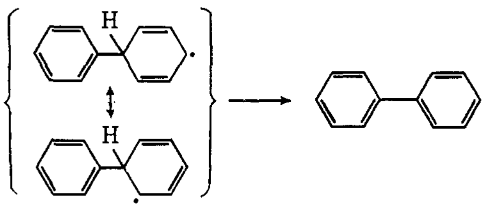
A four-center reaction for the formation of biphenyl from benzene



$+ H_2 \quad \Delta H° = -3$kcal/mole (2)

is attractive, and a second-order rate constant has been calculated.[5] Either this path or the free-radical reaction

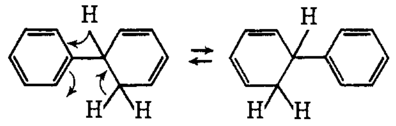
$C_6H_5\cdot + C_6H_6 \rightarrow$



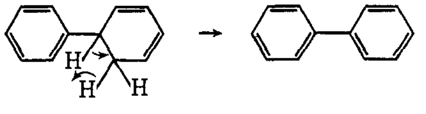
$+ H\cdot$ (3)

would, most simply, effect random loss of one atom from each of the reacting benzene molecules. To be compatible with paths 2 and 3, the assumption of random loss of two atoms from the full hydrogen complement of the two reacting molecules would require equilibration of the hydrogen atoms before the intermediate breaks down to yield biphenyl. Alternatively, this requirement could be satisfied by formation of a complex—perhaps of the donor–acceptor type—or an actual compound, a phenylcyclohexadiene, between two molecules of benzene or other aromatic compound, in which protium and deuterium atoms readily move and exchange.

$2C_6H_6 \rightleftarrows$



, etc. (4)



$+ H_2$ (5)

Such complex formation has been vaguely hinted at as an energy-transfer process in radiolysis studies on benzene.[6] Irradiation of deuterated biphenyls with a cobalt-60 source and analysis of the hydrogen produced led to the conclusion that two processes were involved: a unimolecular decomposition and some sort of bi-

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[3] A. Berthelot, *Jahressber. Fortschr. Chem.*, 540 (1866).

[4] In solution, free-radical arylations have shown no large isotope effect: C. Shih, D. H. Hey, and G. H. Williams, *J. Chem. Soc.*, 1871 (1959); E. L. Eliel, S. Meyerson, Z. Welvart, and S. H. Wilen, *J. Am. Chem. Soc.*, **82**, 2936 (1960).

[5] K. C. Hou and H. B. Palmer, *J. Chem. Phys.*, **69**, 863 (1965).

[6] S. Gordon and M. Burton, *Discussions Faraday Soc.*, **12**, 88 (1952).

Table IV. Pyrolysis of Naphthalene and Biphenyl in Benzene-d_1[a]

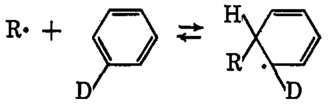
Component recovered	Mass	No. of D atoms	Rel. abundance	
			Naphthalene	Biphenyl
Benzene	78	0	12	15
	79	1	80	78
	80	2	8	7
Naphthalene	128	0	77.7	...
	129	1	19.8	...
	130	2	2.5	...
Biphenyl	154	0	...	74.3
	155	1	...	19.9
	156	2	...	5.1
	157	3	...	0.7

[a] 94.5% benzene-d_1, 5.5% benzene-d_0; 1 mole of naphthalene or biphenyl : 5 moles of benzene.

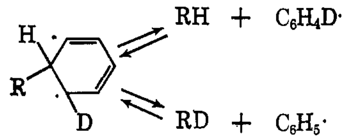
molecular process.[7] The workers studying these systems analyzed only the hydrogen or acetylene produced, not the recovered aromatic compounds. Evidence for the production of cyclohexadiene and more highly hydrogenated derivatives has been found in the mercury-sensitized photolysis of benzene vapor and hydrogen,[8] in the glow discharge of benzene vapor,[9] and in the radiolysis of liquid benzene[10] and of biphenyl.[11]

Hydrogen exchange between benzene molecules may occur to some extent by a series of equilibria involving homolytic cleavage

$$R{-}H \rightleftarrows R\cdot + H\cdot \qquad (6)$$



(3)



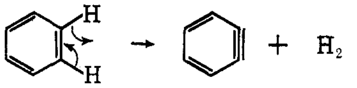
(7)

There may be some contribution from the reaction

$$C_6H_5{-}C_6H_5 \rightleftharpoons 2C_6H_5\cdot \qquad (8)$$

followed by (3) and (7), as demonstrated in the pyrolysis of biphenyl and biphenyl-d_{10} at 438–472° over 2–200 hr.[12] In radiolysis, such C–C bond rupture has been judged unlikely, because but little $C_6H_5^+$ ion results from electron impact on isolated biphenyl molecules in the mass spectrometer[11,13] and because species with even numbers of rings predominate among the polyphenyls formed in radiolysis of biphenyl.[11,14] That most of the exchange in the present work likewise does not involve C–C bond rupture is shown by the pyrolysis of naphthalene and biphenyl separately in benzene-d_1 at 690° and 7.6-sec. contact time. The results are given in Table IV. The considerable amount of exchange that occurred between the naphthalene and the benzene-d_1 furnishes evidence of extensive C–H bond breaking. The almost identical amounts of naphthalene-d_1 and biphenyl-d_1 produced may be significant if, as seems probable, the same process is involved.

Our postulated bimolecular complex or phenylcyclohexadiene intermediate in the pyrolysis of benzene can explain both hydrogen–deuterium exchange and ready intramolecular dehydrogenation to biphenyl without formation of highly energetic free hydrogen atoms. That intramolecular dehydrogenation may be preferred is also shown by the formation of a small but measurable amount (0.2% of the yield of biphenyl) of naphthalene in benzene pyrolysis.[2a] This must involve loss of hydrogen to give benzyne



(9)

followed by the reactions already described.

The similarity of the products obtained from benzene by pyrolysis and by exposure to ionizing radiation is noteworthy and suggests that the radiolysis results can be largely accounted for without involving ionized or electronically excited species as immediate precursors of the products. Electron-impact studies[15] have furnished abundant evidence that those reaction paths with the lowest energy requirements, which would be expected to be favored in thermal processes, are likely to be favored even when enough energy is available to drive almost any conceivable reactions. Thus, the same low-energy reaction paths may well predominate in both pyrolysis and radiolysis of benzene.

Experimental Section

Materials were pyrolyzed under high-purity dry nitrogen in a Vycor tube filled with Vycor beads. Analyses were performed with a Consolidated Model 21-103C mass spectrometer with the inlet system at 250°.

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