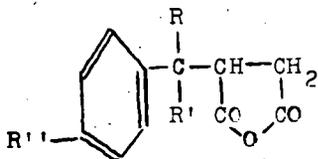


REACTION OF MALEIC ANHYDRIDE WITH AROMATIC HYDROCARBONS
UNDER THE INFLUENCE OF SILENT ELECTRIC DISCHARGE
AT ATMOSPHERIC PRESSURE.

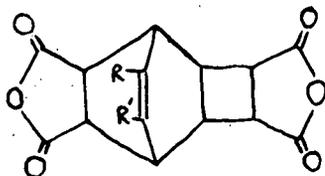
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Maleic anhydride is known to form two classes of adducts with alkyl benzenes, depending on the conditions of excitation. At reflux temperatures and in the presence of catalytic amounts of peroxides adducts of type I are formed (1,2). A free radical chain reaction is assumed involving abstraction of a benzylic hydrogen. The chain length, based on the ratio of product to added peroxide, is 20 to 100.



I (R, R' = H or Me; R'' = Me, Et, i-Pr)



II (R, R' = H, Me, t-Bu, Cl)

At room or somewhat higher temperatures and in the presence of ultra-violet radiation adducts of type II are formed (3 to 8). Excited aromatic molecules or excited charge-transfer complexes of maleic anhydride with an aromatic molecule are claimed to be the reaction intermediates. The addition is sensitized by benzophenone, but the adduct can be formed in the absence of a sensitizer, although at a much lower rate. It appears that the presence of benzophenone is indispensable if sun light is used as the source of exciting radiation (9). It is interesting to note that in this case only benzene forms an adduct II with maleic anhydride, while alkylbenzenes are only partly incorporated in poly-anhydride chains which are formed.

Recently formation of the adduct II of benzene and maleic anhydride under the influence of gamma radiation was reported (10). The adduct is only a minor product of the reaction, corresponding to about 4% of the maleic anhydride spent. The main product is a mixture of poly-anhydrides. These can be considered to arise through a free radical chain similar to the one yielding adducts of type I.

It is then clear that in the system maleic anhydride-benzene (or alkylbenzene) two types of reactions are prevalent, one by free radical chain yielding adduct I or poly-anhydrides, the other by means of excited molecules or charge-transfer complexes yielding adduct II. It was thought of interest to investigate the influence of silent or corona discharge on this system. This type of discharge was chosen because it is easy to maintain at atmospheric pressure.

Experimental.

The discharge apparatus was essentially a modified Siemens ozonizer vertically mounted. It was made of Pyrex glass. A solution of sodium chloride in glycerol circulating in the jacket constituted the ground electrode, while a silver coating in the interior surface of the central

tube served as the high voltage electrode. The reaction mixture was circulated at a high rate from top to bottom through the reactor by means of a custom-made membrane pump constructed of Halon (registered mark of Allied Chemical Corporation). An inert gas, nitrogen or helium, was introduced at the top of the reactor and vented at the bottom through a condenser. The temperature of the reaction mixture was measured at the exit of the discharge. Temperature control was ensured by regulating the temperature of the circulating glycerol solution.

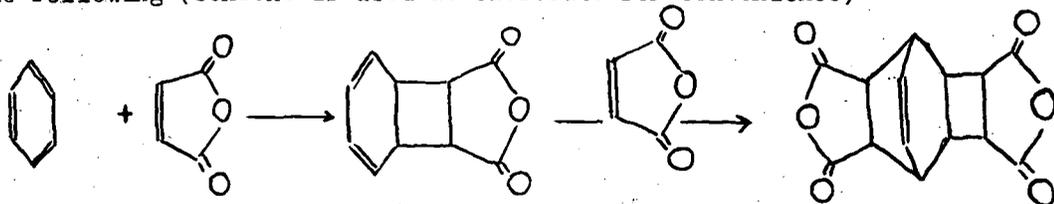
Current at the desired frequencies was produced by an audio-frequency generator (Heathkit Model I7-72) coupled with a 1000 VA custom-made amplifier. It was raised to high voltage by means of a 25 KV transformer. Lower voltages could be obtained by acting on the output of the amplifier. The power input to the system was monitored by means of a watt-meter (Westinghouse Type PY6, specially compensated for high frequency work) at the primary circuit of the transformer.

Eastman White Label chemicals were used without purification. In a typical experiment 29.4 grams of maleic anhydride in 416 ml of cumene were circulated for two hours in the apparatus while the discharge was maintained at a power level of 400 watts. Nitrogen was supplied at the rate of 50 ml/min. The temperature of the reaction mixture was 127° C. The reaction mixture was cooled to 20° C. and the resulting crystals were filtered and washed with 50 ml of cold benzene. Additional crystals were obtained after the mother liquor had been condensed to one third of its initial volume by flash evaporation. The combined product was dried at 50° C. in a vacuum oven. It weighed 5.18 grams and had melting point 255-7° C. Elementary analysis and neutralization equivalent were consistent with formula II ($R = H$, $R' = i\text{-Pr}$). The infra-red spectrum showed absence of aromatic character. Flash evaporation of the unreacted cumene and maleic anhydride left 23.0 grams of a viscous residue which had neutralization equivalent corresponding to a mixture of a 1:1 and 2:1 adduct of maleic anhydride and cumene. It was assumed that it contained adduct of formula I ($R = R' = \text{Me}$) together with products of further condensation with maleic anhydride. Infra-red and NMR spectra were consistent with this assumption.

Similar results were obtained using benzene, toluene, and ethylbenzene as substrates. Chlorobenzene and nitrobenzene failed to yield a crystalline product. The experimental conditions and the results are summarized in table I.

Discussion.

It is apparent from the present results that maleic anhydride forms an adduct of type II with benzene and alkylbenzenes under the influence of silent discharge. The generally accepted path of formation of II in photochemical (3) or gamma-radiation induced (10) reaction is the following (benzene is used as substrate for convenience)



It is reasonable to expect that the same path is followed also in the present case of discharge excitation. Since the rate of formation of adduct II is independent of the concentration of maleic anhydride (experiments 2 and 4) it is concluded that the formation of the intermediate monoadduct is the rate-determining step. The same conclusion has been reached in the photochemical formation of adduct II (3,4).

Adduct II is not, however, the only product formed in the reaction; a considerably larger amount of resinous material (tabulated as adduct "Type I") is also formed in all cases. This material arises from a free radical reaction similar to the one giving rise to adduct I in peroxide-initiated reactions. The chain length of these reactions is about 20 to 100, as mentioned earlier. On the other hand it has been shown that the quantum yield of adduct II formed in photochemical reaction is about 0.1 (4). Since in the present experiments adduct II is formed in amounts about one quarter of the amount of "type I" adduct although about ten excited molecules, or charge-transfer complexes, are necessary to produce one molecule of II, while one free radical will produce 20 to 100 molecules of I, it must be concluded that the great majority of active species in the liquid phase in contact with the discharge are excited molecules and not free radicals. In fact it can be estimated that 98% to 99% of the active species are excited molecules. The absence of free radicals as important reaction intermediates has also been deduced by product analysis in the microwave glow discharge of aromatics in helium, (11).

In the photochemical reaction benzene forms an adduct II at a higher rate than the alkylbenzenes, which in turn react in relative rates indicative of steric hindrance. No such effect was observed in the present work, as shown by the power yields in the table. These yields are also measures of the rate of formation of adduct II since roughly equal power levels of discharge were maintained in all cases.

Comparison of runs 1 and 2 shows that formation of adduct II is favored at the lower frequency with a correspondingly higher potential difference applied across the electrodes. Although the electric field strength between the dielectric surfaces is not necessarily proportional to the externally measured potential difference (12), it appears that electrons of higher average energy favor the production of adduct II, as evidenced by the fact that the rate of formation of II is higher in a helium than in a nitrogen atmosphere (runs 4 and 5). It is known that the average electron energy for equal field strength is quite larger in the former gas (13). Of course the presence of organic vapors modifies the electron energy distribution but it is reasonable to expect that some difference still exists.

The mechanism of energy transfer cannot be deduced with certainty from the present data. Comparison of yields at two temperatures (runs 2 and 3) shows higher yield at the higher temperature, a fact which may be interpreted as meaning that benzene vapors in the discharge are excited by collision with electrons: at the higher temperature the concentration of benzene in the gas phase is higher. While this conclusion may be correct it is not unambiguous because of mechanical difficulties at the lower temperature, arising from the fact that adduct II was sparingly soluble in benzene at this temperature and quickly coated the dielectric surfaces where it was partly decomposed. Another way of excitation would involve bombardment of the liquid phase with electrons generated in the discharge. This method of excitation has been shown to prevail in the discharge-induced oxidation of acidified water and ferrous

ion (14). Excitation by collision with excited nitrogen or helium cannot be an important process, considering that the first excited state of helium contains 19.81 ev of energy (15). Collision with such a species would result in extensive fragmentation of an organic molecule, whereas the present results point to the fact that free radical initiation is very limited in this system.

Table I. Condensation of maleic anhydride with benzene and alkylbenzenes under the influence of silent electric discharge.

Number	Charge, gas	Frequ. Kc/sec	Potent. KV.	Temp. C.	Adduct, grams		Yield of II mmole/kw-hr	m.p. C.
					Type I	II		
1	350 ml benz. 50 g MA, N ₂	8.0	10.0	78	25.3	2.12	12.0	
2	350 ml benz. 51 g MA, N ₂	3.6	13.0	75	18.0	3.40	26.5	
3	350 ml benz. 49 g MA, N ₂	3.6	12.5	37	13.2	2.19(a)	15.6	
4	380 ml benz. 12 g MA, N ₂	3.6	13.0	74	14.5	2.77	26.2	
5	380 ml benz. 13 g MA, He	3.6	13.0	75	15.1	4.16	33.3	355-57
6	380 ml tolu. 13 g MA, He	3.6	13.0	82	30.0	4.79	30.4	245-60
7	268 ml etbz. 29 g MA, N ₂	3.6	13.0	121	25.1	7.35	36.0	260-61
8	416 ml cume. 29 g MA, N ₂	3.6	13.0	127	23.0	5.18	29.8	255-57

(a) The product was brown.

Abbreviations: MA, benz, tolu, etbz, cume denote correspondingly maleic anhydride, benzene, toluene, ethylbenzene and cumene.

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