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Reactions of Benzoin and Benzil over Alumina: Decarbonylation of α-Diketones

In continuation with the studies (*1*, *2*) on the disproportionation of benzyl alcohol, the reaction of benzoin (an α-ketoalcohol) was carried out on alumina. Benzophenone and diphenylmethane were formed, in addition to normal disproportionation products like benzil and deoxybenzoin. With a view to establish the reaction sequence of benzoin, benzil was passed over alumina at 400°C. Interestingly benzophenone was formed as the major product along with trace amounts of diphenylmethane.

$$\begin{aligned}\phi\mathrm{CHOHCO}\phi \xrightarrow[400^\circ\mathrm{C}]{\mathrm{Al_2O_3}} \;& \phi\mathrm{COCH_2}\phi \\ &+ \phi\mathrm{COCO}\phi + \mathrm{H_2O} + \mathrm{OCH_2}\phi \\ &+ \phi\mathrm{CO}\phi + \mathrm{CO_2} + \mathrm{CO}\end{aligned}$$

$$\begin{aligned}\phi\mathrm{COCO}\phi \xrightarrow[400^\circ\mathrm{C}]{\mathrm{Al_2O_3}} \;& \phi\mathrm{CH_2}\phi + \underset{\text{(major)}}{\phi\mathrm{CO}\phi} \\ &+ \mathrm{CO} + \mathrm{CO_2}\end{aligned}$$

The present paper deals with the reaction sequence of benzoin and the nature of the decarbonylation of benzil.

Alumina catalyst was prepared (*1*) by the hydrolysis of aluminum isopropoxide by the moisture present in air. Sodium ion-doped alumina catalysts were prepared by stirring alumina with a standard sodium hydroxide solution. Thoria and magnesia were prepared by the hydrolysis of the corresponding nitrates by aqueous ammonia. The precipitated hydroxides were dried at 120°C and then calcined at 600°C. The products were analyzed using a SE-30 column (5% on Chromosorb, 60–80 mesh, acid-washed, with $\frac{1}{8}$-in. diam., 6 ft. length) and TC detector.

Results of reactions of benzoin, benzil, and substituted benzils are given in Table 1. It has been reported (*3*) that diphenylacetic acid, diphenylmethane, and carbon dioxide were formed in the reaction of benzoin with 60% phosphoric acid supported on alumina or silica at 290°C. Under our experimental condition, no diphenylacetic acid was detected in the reaction of benzoin on alumina. However, diphenylacetic acid when passed over alumina gave diphenylmethane quantitatively at 400°C. The catalytic disproportionation of benzoin to benzil and deoxybenzoin ($\phi\mathrm{COCH_2}\phi$) has been reported (4) to take place during the gas chromatographic analysis. However, no such reaction was noticed under our gas chromatographic conditions. In the reaction of benzoin over alumina, benzophenone, diphenylmethane, benzil, deoxybenzoin, carbon dioxide, and carbon monoxide were formed. Benzophenone was formed as the major product in addition to carbon dioxide, carbon monoxide, and trace amounts of diphenylmethane in the reaction of benzil over alumina. The identities of carbon dioxide and carbon monoxide were established by the ir spectra of the gases formed in the reactions [CO: $\gamma = 2165\ \mathrm{cm^{-1}}$, $\mathrm{CO_2}$: $\gamma = 2347$ and $667\ \mathrm{cm^{-1}}$]. The decarbonylation of benzil to benzophenone did not take place when it was passed over glass pieces at 400°C (in the absence of alumina). Thus it appears that the reaction of benzil to benzophenone is catalytic in nature. Added water had no influence on the product distribution of benzil. However, added methanol increases the formation of diphenylmethane leading to the suppression of benzophenone. Thus based on these observations and literature reports (*3*, *4*), the probable reaction sequences of benzoin can be shown by Scheme 1.

Results of the reaction of substituted ben-

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TABLE 1

Reactions of Benzoin, Benzil, and Other Compounds over Alumina

Substance No.	Reactant	Total conversion (%)	$\phi CH_2\phi$	Product distribution in mole %[a]			
				$\phi CO\phi$	$\phi COCO\phi$	$\phi CH_2CO\phi$	Others
1	Benzoin[b]	95	17	21	11	43	3
2	Benzil	80	5	70	—	—	5
3	Benzil + H_2O[c]	62	6	68	—	—	9
4	Benzil + CH_3OH[c]	96	40	51	4	Trace	1
5	Benzil over glass pieces	—	—	—	100	—	—
6	4,4′-Dimethylbenzil	65	4,4′-Dimethyldiphenylmethane	3	4,4′-Dimethylbenzophenone	61	1
7	4,4′-Dimethoxybenzil[d]	40	4,4′-Dimethoxydiphenylmethane	>1	4,4′-Dimethoxybenzophenone	15	25
8	Diphenylacetic acid	100	Diphenylmethane	98	—		2
9	Benzilic acid[e]	90	Diphenylmethane	16	Benzophenone	18	56
10	Benzil + 4,4′-dimethylbenzil[f]	71 (of benzil)	Diphenylmethane	2	Benzophenone	65	4
		60 (of 4,4′-dimethylbenzil)	4,4′-Dimethylphenylmethane	>1	4,4′-Dimethylbenzophenone 4-Methylbenzophenone	52 0	8

Note. Weight of alumina: 2 g. Temperature: 400°C. Reactant: 1 × 10^{-2} mole made up to 20 ml in benzene. Flow rate: 20 ml/hr.

[a] In the reactions of benzil and benzoin, carbon dioxide and carbon monoxide were formed.

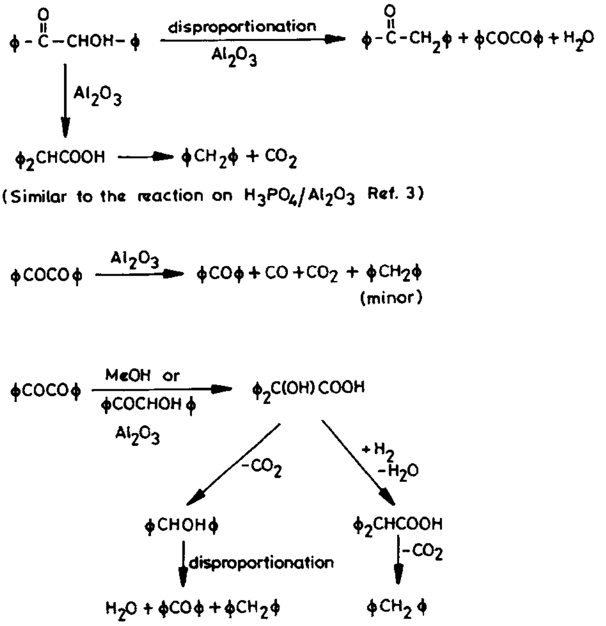
[b] Reactant: 1 × 10^{-2} mole, made up to 50 ml. Flow rate: 33 ml/hr.

[c] Reactant: 2 × 10^{-2} mole (1:1 mole ratio).

[d] Reactant: 0.5 × 10^{-2} mole made up to 20 ml in benzene. Flow rate 20 ml/hr.

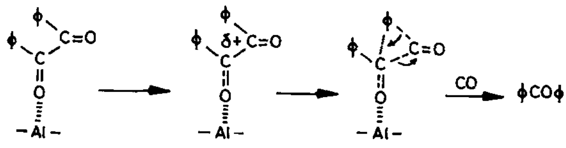
[e] Reactant: 0.25 × 10^{-2} mole made up to 50 ml in benzene. Flow rate: 33 ml/hr.

[f] Reactant: 1 × 10^{-2} mole (1:1 mole ratio) made up to 20 ml in benzene. Flow rate: 20 ml/hr. Due to difference in the solubility of the reactants in benzene, reactants were taken in different mole fractions as indicated above.

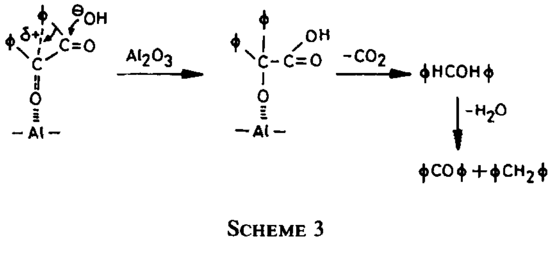


(Similar to the reaction on H_3PO_4/Al_2O_3 Ref. 3)

SCHEME 1



SCHEME 2



SCHEME 3

zils are also given in Table 1. From the results it is clear that substituted benzils were less reactive than benzil itself. To understand the nature of the decarbonylation of benzil, whether inter- or intramolecular, reaction of benzil with 4,4′-dimethylbenzil was carried out (Table 1, No. 10). The presence of benzophenone and 4,4′-dimethylbenzophenone and the absence of crossed decarbonylation product, namely 4-methylbenzophenone, showed that the decarbonylation is intramolecular in nature. The decarbonylation of benzil to benzophenone and the formation of diphenylmethane and carbon dioxide from benzil can be explained by Schemes 2 and 3.

TABLE 2

Reaction of Benzil over Oxide Catalysts

Substance No.	Catalysts	Total conversion	Products distribution in mole %		
			$\phi CH_2\phi$	$\phi CO\phi$	Others
1	Al_2O_3	70	5	62	3
2	Na/Al_2O_3 (1.9%)	89	3	82	4
3	Na/Al_2O_3 (0.72%)	81	2	78	1
4	Na/Al_2O_3 (0.19%)	75	3	70	2
5	MgO	20	Trace	15	5
6	ThO_2	16	Trace	13	3
7	$Ba(OH_2)_2$	2	Trace	Trace	2

Note. Catalyst weight = 2 g. Reactant: 1×10^{-2} mole of benzil made up to 10 ml in benzene. Temperature: 400°C. Flow rate: 10 ml/hr.

Along with other products, diphenylmethane and benzophenone were formed in the reaction of benzilic acid over alumina at 400°C. Apart from these observations no experimental details are available to support the mechanism involving adsorbed benzilic acid (Scheme 3). No benzilic acid was detected in the reaction of benzil over alumina.

Reactions of benzil were carried out on sodium-impregnated alumina, thoria, magnesia, and barium hydroxide (Table 2). From the results it is clear that as the concentration of sodium increases the activity of alumina toward decarbonylation of benzil also increases. Magnesia and thoria exhibit more or less the same order of activity but very low compared to alumina. In barium hydroxide the reaction does take place however to an insignificant extent.

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