2. The yield of stilbene and 1,3-diphenylbutene, the dimerization product of styrene, in the presence of pyridine is lowered according to the substitution of phenyl groups on the phosphorus ligand L by alkyl (ethyl, cyclohexyl) groups.

3. Change of triphenylphosphine to phenylethylphosphines and tricyclohexylphosphine in the hydride complex $HNi(X)(PR_3)_2$, the catalytic activity of which falls in the order $X = Cl^- \gg Br^- > I^-$, favors the dimerization of styrene in the absence of pyridine.

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METHYLATION OF PHENOL BY METHYL FORMATE

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547.562.1

The development of the industrial manufacture of formic acid from CO and H_2O has also made methyl formate (MF), an intermediate in this high-tonnage synthesis, available [1]. Unlike that of many other esters, the reactivity of MF has been studied insufficiently. For this reason, we investigated the reaction of MF with phenol in the presence of acid catalysts. We can assume that in this case reactions are possible with the participation of hydrogen both in the hydroxyl group and of the aromatic ring.

EXPERIMENTAL

The MF was boiled over anhydrous $MgSO_4$ and distilled with a fractionating column. Freshly distilled phenol was used. Fused $ZnCl_2$, $C_4F_9SO_3H$, $p\text{-}CH_3{-}C_6H_4SO_3H \cdot H_2O$, tungstosilicic acid $H_8[Si(W_2O_7)_6] \cdot xH_2O$, tungstophosphoric acid $H_7[P(W_2O_7)_6] \cdot xH_2O$, KU-23, and zirconium oxide were used as catalysts [2]. The zirconium oxide was prepared by dissolving ZrO_2 with boiling in concentrated H_2SO_4 and hydrolyzing the obained zirconium sulfate with an aqueous ammonia solution. The zirconium hydroxide was filtered, washed with water, and dried for 10-15 h at 373 K. The ground hydroxide was treated with a 0.5 M H_2SO_4 solution (30 ml of a 0.5 M H_2SO_4 solution per 2 g of $Zr(OH)_4$) and calcined in a muffle furnace at 773-923 K.

The experiments were carried out in an autoclave made of stainless steel with an electrically heated 50 cm^3 vessel equipped with a reflux condenser, manometer, and sampling valve. The temperature in the reaction zone was monitored with a thermocouple connected to a KSP-005 potentiometer. The reaction products were analyzed with a Tsvet-100 chromatograph with a thermal-conductivity detector and a 2 m × 3 mm column filled with Polysorb-1. The feed

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TABLE 1. Catalytic Activity of Various Catalysts in the Reaction of Methyl Formate with PhOH (0.05 mole of PhOH, 0.6 mole of MF, 3 h, 448-453 K, and $6 \cdot 10^6$ Pa)

Expt. No.	Catalyst	Amount of catalyst, g (mole)	Degree of conversion of phenol, %	Selectivity, %		Other products
				anisole	salicylaldehyde	
1	Without catalyst	–	–	–	–	a
2	$ZnCl_2$	13,7 (0,1)	25,5	60	40	b
3	p-CH_3–$C_6H_4SO_3H$	4,3 (0,025)	3	100	–	c
4	ZrO_2	1,5 (0,012)	21	100	–	b
5	Tungstophosphoric acid	2,5 (0,0008)	13,5	100	–	b
6	Tungstosilicic acid	2 (0,0007)	11	100	–	b
7	$C_4F_9SO_3H$	6,3 (0,02)	5	100	–	c
8	KU-23	6,0	–	–	–	a
9	Al_2O_3	5,1 (0,05)	–	–	–	a
10	$Zn(CH_3COO)_2$	8 (0,04)	–	–	–	d
11	$Zn(C_6H_5COO)_2$	9 (0,03)	–	–	–	e

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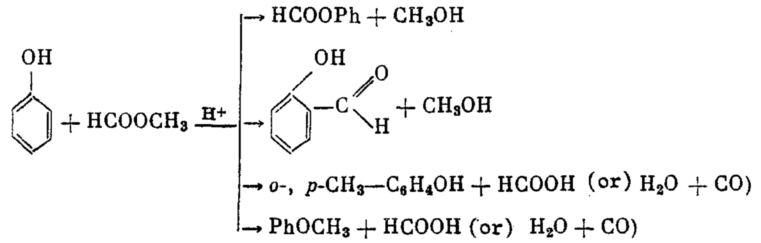
[a] Reaction products were not observed.
[b] Insignificant amount of CO.
[c] Decomposition of MF into CO and methanol.
[d] Methyl acetate (1 mole/mole of $Zn(CH_3COO)_2$).
[e] Methyl benzoate (1 mole/mole of $Zn(PhCOO)_2$).

rate of the carrier gas (He) was 50 cm^3/min, and the conditions of the programmed temperature rise were from 393 to 548 K at a rate of 18 K/min.

RESULTS AND DISCUSSION

In principle, under acid-catalysis conditions, the attack of phenol by protonated MF can lead to the formation of anisole or phenyl formate (products of replacement of the H atom in the hydroxyl) and also salicylaldehyde or o- or p-cresols (with substitution in the aromatic ring)



(1)
(2)
(3)
(4)

Phenyl formate was formed in none of the experiments (Table 1). The reaction is probably thermodynamically hindered because the formyl and phenyl groups in the obtained ester compete with each other for reaction with the unshared electron pair of the O atom of the ester group, whereas in the starting compounds this type of bonding is not hindered.

Thermodynamic factors also prevent the formation of salicylaldehyde because, according to the data of [3], $\Delta H^\circ_{298} \simeq 95.6$ kJ/mole for reaction (2) at $\Delta S^\circ_{298} \simeq 0$ makes it practically unattainable.

The appearance of salicylaldehyde in the catalysis by $ZnCl_2$ is apparently a consequence of a stoichiometric process, e.g.,

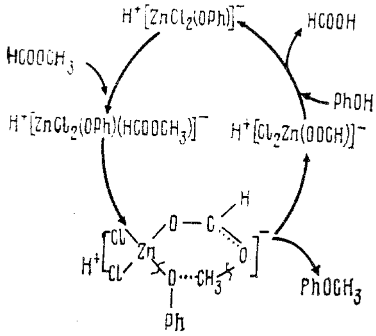
$$ZnCl_2 + HCOOCH_3 + C_6H_5OH \rightarrow ZnCl(OCH_3) + C_6H_4(OH)CHO + HCl$$

The recovery of HCl and the irreversible (under the experimental conditions) alcoholysis (or hydrolysis) of the starting form of the catalyst, which becomes a consumable reagent under these conditions, provide thermodynamic conditions for the occurrence of formylation. We found cresols (primarily the ortho isomer) only in the products of the reaction of MF with PhOH in the presence of Al_2O_3 above 573 K. Under the conditions of the experiments, the results of which are given in Table 1, the yield of these products was extremely low.

The main direction of the catalytic reactions observed under the conditions of our experiments is the formation of anisole. In the reaction of MF with phenol, cleavage of the Ph—OH bond is apparently precluded, which indicates the occurrence of cleavage of the CH_3—O bond. The cleavage of the alkyl—O bond in the ester is a rather unusual phenomenon, encountered previously only in the case when, at the C atom of the alkyl or aralkyl radical, there are groups capable of stabilizing an intermediately appearing carbonium ion [4, 5]. The observed phenomenon cannot be explained by hydrolysis of MF by water impurities and by the reaction of phenol with the resulting CH_3OH because the latter cannot methylate phenol under the conditions of our experiments. Apparently, the increase in the mobility of the methyl group is due to coordination of MF at the central atom of the catalyst.

As is evident from the data given in Table 1, the greatest activity in the reaction of MF with phenol was exhibited by ZnCl, sulfuric acid-treated ZrO_2, and heteropoly acids. Fluoroalkanesulfonic acids and p-toluenesulfonic acid exhibited significant activity, but Al_2O_3 and KU-23 exerted no catalytic effect. Thus, in general, the protic catalysts were less active than the aprotic ones.

It can be assumed that in the catalysis by Zn and Zr compounds, the central atoms of which tend to form strong bonds with oxygen-containing ligands, there is coordination of the phenol at the metal atom with the formation of a $[ZnCl_2OPh]^-$-type phenolate complex. The reaction of such a complex with MF, possibly also including the coordination of this ester, ends with the formation of a formate complex, which, in the reaction with phenol, again regenerates the coordination compound responsible for the reaction.



Within the framework of the assumed mechanism, the catalytic reaction includes inner-sphere nucleophilic substitution, in which the coordinated phenolate ion replaces the weaker nucleophile, the C atom of the CH_3 group of the coordinated MF. For confirmation of the proposed mechanism, we need, above all, information on the reaction kinetics. However, there are a number of other factors indirectly supporting this scheme.

Thus, it is obvious that for the occurrence of such a scheme the ligands at the central atom should not prevent the coordination of the reagents and, in addition, should react with neither the phenolate ion nor MF. Indeed, in the case of zinc acetate and benzoate the bidentately coordinated acido ligands screen the central atom, preventing coordination of the reagents. As a result of this, reaction (4) is not observed (phenol is not consumed), and the MF, reacting with the starting complex, alkylates the acido ligand with the formation of methyl acetate and methyl benzoate, respectively.

$$\mathrm{Zn(OCOR)_2 + HCOOCH_3 \rightarrow Zn(OCOH)_2 + RCOOCH_3}$$
$$\mathrm{R = CH_3,\ Ph.}$$

Neither aniline nor N,N-dimethylaniline reacts with MF under the conditions of the O-alkylation of phenol. Apparently, aniline, more basic than phenol, cannot be deprotonated in the reaction with the catalyst. Under more severe conditions (573 K), aniline is converted to N,N-dimethylaniline.

CONCLUSIONS

In the presence of $ZnCl_2$ and ZrO_2, methyl formate methylates phenol to anisole with a high degree of selectivity.

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KINETICS OF THE THERMAL DECOMPOSITION OF N,N-(DINITRO)ALKYLAMINES

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At the present time, vast research material is available on the kinetics of thermal decomposition of mononitroamines [1]. However, with the exception of [2], there is no information in the literature on the thermal decomposition of N,N-dinitroamines, even though this information is important in acquiring a general knowlege of the thermal decomposition of nitro compounds and in understanding the relationship between the reactivity of nitroamines and their structure.

The current work is dedicated to the gas-phase kinetics of the decomposition of dinitroamines with the general formula $RN(NO_2)_2$, where R = CH_3, C_2H_5, n-C_3H_7, n-C_4H_9.

EXPERIMENTAL

Dinitroamines were synthesized and purified as described in [3, 4]. Kinetic measurements were conducted manometrically using Bourdon glass membrane manometers. The volume of the reaction vessel was approximately 80 ml. In order to ensure that the reaction is in the gas phase, the initial pressure readings p_i^0 were taken under lower pressure of saturated steam. They were also measured using glass manometers. The saturated steam pressure readings at different temperatures allowed the determination of the enthalpy of vaporization of the compounds studied according to the equation

$$p = A\exp(-\Delta H_{\text{vap}}/RT) \qquad (I)$$

The kinetics of all the reactions studied, up to higher-order conversions, followed first-order equations. In some cases, deviation from the first order was observed at low temperatures; this is discussed in more detail in [5]. These deviations were not taken into account in the computation of rate constants. The activation parameters of decomposition and enthalpy of vaporization were calculated using the least-squares method. The confidence limits were computed using the Student distribution with 0.95 probability.

Table 1 shows data on the saturated steam pressure of the dinitroamines. Within the margin of error, the enthalpy of vaporization of $CH_3N(NO_2)_2$ is in agreement with values measured using Calvet microcalorimeter [6]. As can be seen in Table 2, k is independent of p_i^0. The sevenfold change in specific surface of the reaction vessel (the addition of glass filling) also did not affect the values of the constants. The influence of addition of various gases on the decomposition kinetics was studied on $C_2H_5N(NO_2)_2$. The data in Table 3 show that these additives do not affect the reaction kinetics. The decomposition of dinitroamines in solution was also studied in a number of experiments. It was shown

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