637. *Organic Fluorides. Part II. The Effect of Metals on the Fluorination of Hydrocarbons.*

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The catalytic effect of a number of transitional elements on the vapour-phase fluorination of benzene has been investigated. Gold-plated copper turnings appear to be the most effective.

In Part I (preceding paper) it was shown that silver-plated copper turnings had a pronounced beneficial effect on the fluorination of hydrocarbons (see also Cady *et al.*, *Ind. Eng. Chem.*, **1947**,

Catalyst.	Temp. of re-actor.	Total wt. of F_2, g./hr.	Total wt. of C_6H_6 used (g.).	Nitrogen dilution, l. per hour.		Dur-ation of expt. (hrs.).	Wt. of product (g.).			Total wt. (g.) crude product.	Fractionation of product.			Yield of C_6F_{12} on C_6H_6 used (%).	State of catalyst on removal from reactor.
				F_2.	C_6H_6.		Trap A.	Trap B.	U-tubes.		decomp. products, b. p. 30—47°.	crude C_6F_{12}, b. p. 47—60°.	partly fluorinated and polymeric products, b. p. >60°.		
Ag-plated Cu turnings (*ca.* 4 kg.)	200°	16	77·8	11·5	10	25	15	28	100·5	143·5	8·2	53·6	64·5	18	Bright metallic surface which became black immediately on contact with air.
	265	16	37·1	10·5	10	11·5	14	15	68·0	97·0	6·4	37·7	41·3	26·4	
	310	16	36·7	10·5	10	11·5	3	3·5	66·0	72·5	12·5	28·1	23	19·9	
Cu turnings (*ca.* 4 kg.)	210	16	35	9·5	9	11	6·5	10·2	49·1	65·8	8·25	21·8	29	16·2	Bright metallic surface.
	265	16	30·6	9·5	9	9·5	13·3	4·4	64·8	82·5	12·5	34·6	27·8	29·4	
	310	16	41·9	7·5	7·5	10·5	0·6	7·1	76·5	84·2	26	29·8	22·8	18·5	
Au-plated Cu turnings (*ca.* 4 kg.)	200	16	38·5	10·5	10	10	4	11	53	68	2·5	31·5	29	21·3	Dark maroon colour, seemed quite stable in air.
	260	16	33·2	10·5	10	9·5	8·5	12·5	63	84	0	44·6	33	35	
	320	16	45·4	10·5	10	12	8	10·5	112	130·5	11·5	70·2	41	40·2	
Ni-plated Cu turnings (*ca.* 4 kg.)	200	16	28·8	11·5	10	9	4	13	49	66	8·5	22·5	30·9	20·3	Bright metallic surface; no change.
	265—270	16	35·8	11·5	11	11·5	10·5	10	75·5	96	14·7	31·3	33·6	22·7	
	305	16	38·5	11·5	11·5	13	5	7	86	98	15·1	42·4	32·4	28·6	
Co-plated Cu turnings (*ca.* 4 kg.)	210	16	38·5	11	10	11	10	15	50·5	75·5	6·8	29·9	32·1	20·2	Catalyst at top of reactor had become a pale pinkish-blue. That in lower part unchanged.
	265	16	35·8	10·5	10	10	21·5	0·5	66	88	7	38·7	32·6	28·1	
	310	16	40·2	10	9·5	10	21·5	3·5	84·5	109·5	9·6	57·2	31·9	37	
Brass turnings (*ca.* 4 kg.)	200	16	33·2	14	5·5	9	2·6	12	49	63·6	7	30·6	22·5	24	No obvious change.
	260	16	38·5	14	7	11	5·5	4·5	67·6	77·6	25·1	34·8	10·3	23·5	
	300	16	41·9	12·5	5·5	11	1·5	1·5	92	95·0	19·8	43·3	23·6	26·9	
Hg-coated Cu turnings (*ca.* 4 kg.)	200	14	30·6	14	5·5	11	5·9	4·9	37·6	48·4	3·5	19·4	20·7	16·5	Hg converted into white powder (HgF_2). Some of this had fallen off, leaving small bare patches of Cu.
	260	16	40·2	14	5·5	11·5	2·1	0·9	44·8	47·8	12·5	15·8	13·1	10·2	
	310	16·8	39·3	12·5	7·5	10·5	4·7	4·3	49·7	58·7	17·8	20·4	14·4	13·5	
Rh-plated Cu wire (*ca.* 1 kg.)	200	16	34·1	10	9·5	9·5	1·5	5·7	44·5	51·7	22·1	12·4	12·5	9·5	No change.
	265	16	35·8	10	9·5	9	0·5	7·5	63	71	21·3	23·3	20	16·9	
	310	16	28·8	10·5	10	9	2·0	4·3	58·7	65	15·3	24·8	20·1	22·4	
Cr-plated Cu wire (*ca.* 1 kg.)	210	16·8	38·5	9	9	11	6·5	5	43	54·5	5·2	24·6	18·3	16·6	No change.
	260	16·8	29·1 [1]	11	7	10	1·3	0·9	29·7 [2]	32	12·3	7·5	9·7	6·7	
	300	16·8	34·2 [3]	13	6·5	11	0·9	1·1	34·5 [4]	36·5	16·5	8	10·8	6·1	
Steel wool (reactor packed tightly)	210	16·8	36·7	15	6·5	10·5	5·8	2·3	42	50·1	15·4	12·8	16·1	9·1	Bright metallic surface. Slight attack on catalyst at top of reactor.
	260	16·8	34·1	12	6·5	9·5	3·9	4·8	52	60·7	16·7	20·9	16·3	15·9	
	300	16·8	35·8	14	7	11	0·6	0·4	54·2	55·2	23·8	16·7	7·4	12·1	

[1] 37 G. were carried into reactor, but 8 g. were recovered from U-tubes.

[2] Together with 9·8 g. of an upper layer which on distillation gave 8 g. of benzene.

[3] 43·7 G. were carried into reactor, but 9·5 g. were recovered from U-tubes.

[4] Together with 11·7 g. of an upper layer which on distillation gave 9·5 g. of benzene.

39, 290). The moderating influence of copper gauzes on the reaction between fluorine and organic compounds at relatively low temperatures was first noted by Fedenhagen and Cadenbach (*Ber.*, 1934, **67**, 928) and later applied extensively by Bigelow and his co-workers (see, *e.g.*, *J. Amer. Chem. Soc.*, **1941**, **63**, 2792); all these experiments, however, were characterised by the low yields and extensive decomposition of the products.

Recent studies have established, however, the surprising fact that the yields of fluorocarbons are greatly improved by fluorinating the hydrocarbons at comparatively high temperatures (200—300°) in the presence of a large metal surface. This work shows that the conversion of hydrocarbons into the corresponding fluorocarbons by direct fluorination at these higher temperatures is facilitated, not only by copper and silver, but also by other transitional elements. In the experiments reported herein benzene was used as the standard substance in order to ascertain the relative effectiveness of the catalysts. Gold-plated copper turnings were the most effective catalyst in the production of perfluoro*cyclo*hexane and were later put to extensive use. Cobalt approached gold closely as a catalyst; silver, nickel, copper, and brass were next best, whilst mercury, chromium, rhodium, and iron were much inferior.

It is important that the metal catalyst be plated on a metal, such as nickel or copper, relatively inert to fluorine. This is especially desirable if the catalyst gives a porous, and not a particularly strongly adhering, fluoride, otherwise swelling occurs during the transformation of the metal into the fluoride; this may result in channelling or even complete blockage of the reaction vessel, as occurred when an attempt was made to utilise silver turnings.

EXPERIMENTAL.

The apparatus was identical with that used in our initial experiments (see preceding paper and Cady *et al.*, *Ind. Eng. Chem.*, 1947, **39**, 290). The reactor was charged with copper turnings (*ca.* 4 kg.) on which the catalyst was plated (electrically). With certain metals such as chromium and rhodium, it was somewhat difficult to plate the turnings; in these cases, the catalyst was plated on fine copper wire. The standard substance used in all experiments was benzene (thiophen-free). Reaction conditions for each catalyst were kept as near constant as possible. Thus, in almost every experiment, the fluorine was diluted with about 10 l. of nitrogen per hour, while the benzene was carried into the reactor by nitrogen flowing at the same rate. If equal dilutions of fluorine and benzene with nitrogen could not be maintained, the volume of nitrogen diluting one of the reactants (usually fluorine) was altered so that the total dilution was approximately the same in each experiment. The volume of fluorine was adjusted by altering the current passing through the cell (current efficiency, 65%), so that approximately the theoretical amount required to convert the benzene into hexafluoro*cyclo*hexane was added. By keeping these factors (input of fluorine, benzene, and nitrogen) as nearly constant as possible, and by carrying out experiments on each catalyst at 3 different temperatures (210°, 265°, and 310°), it was felt that reasonably accurate estimates of their catalytic activity could be deduced. It is very probable that, by variation of all the different factors involved, better yields of hexafluoro*cyclo*hexane could be obtained, but it is believed that the relative catalytic powers would not be altered to any great extent.

Before performing a series of experiments, the apparatus was tested for leaks by introducing benzene into the reactor in a stream of nitrogen. It was found that, under optimum conditions, for every 20 c.c. leaving the reservoir, 18 c.c. could be collected in the U-tubes. When the vapour left in the apparatus and slight losses in the scrubber were allowed for, this was thought to be quite reasonable. In any case, since these standard conditions held for each experiment, such a loss, if constant, is of no importance in the consideration of relative results.

In every case the products in the U-tubes and traps A and B were combined, dried (P_2O_5), and fractionated. The results were calculated from the yield of crude perfluoro*cyclo*hexane isolated by this one fractionation.

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