316. *The Reaction of Cyanogen and Related Nitriles with* 1 : 3-*Dienes. Part II. Catalysis of the Reaction of Cyanogen and Related Nitriles with* 1 : 3-*Butadiene.*

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The catalysis of the cyclisation reaction between organic nitriles and dienes to form pyridinic products is reported. Of the catalysts tested a mixture of chromium oxide and activated alumina was most promising. The activity–composition relationship of this catalyst was studied, as well as its activity in the cyclisation when only the nitrile was varied. The region of enhanced activity found indicates there is a promoter type of activity in this mixed catalyst. In the presence of the catalyst, the order of the space-time yields for these reactions has been reversed by comparison with that observed for the uncatalysed reactions, and the order now seems to be related to the polarisability of the organic nitrile.

In a search for catalysts for the reactions described in the preceding paper, the preliminary activity measurements were made on the butadiene–benzonitrile reaction. The ratio of the space-time yield in the catalysed to that in the uncatalysed reaction, under the same conditions of space velocity, temperature, etc., was taken as the measure of the activity of the catalyst. The measurements were carried out at a relatively low temperature (400°) since the cyclisation is thermodynamically more favoured in this range, and at fairly rapid space velocities to minimize complications from secondary reactions. The catalysts investigated, and the activities found, in the preliminary search were as follows :

Catalyst.	Activity.
(Z–1), Activated alumina	5·08
(Z–2), 10% Nickel on alumina	3·76
(Z–3), Phosphoric acid on kieselguhr	1·91
(Z–4), Phosphoric acid on alumina	3·55
(Z–5*a*), 13% Chromium oxide on alumina	11·0
(Z–6), 10% Iron oxide on alumina	6·96
(Z–7*a*), Chromium oxide	1·91
(Z–5*b*), 5% Chromium oxide on alumina	17·8

The results indicate that catalysts favouring cyclisation and dehydrogenation (Taylor and Turkevich, *Trans. Faraday Soc.*, 1939, **35**, 921; Rideal and Herington, *Proc. Roy. Soc.*, 1945, *A*, **184**, 447; Steiner, *J. Inst. Petr.*, 1947, **33**, 410; Kline and Turkevich, *J. Amer. Chem. Soc.*, 1944, **66**, 1710) are the most active for this reaction. The mixed catalyst, chromium oxide–activated alumina, was chosen for further investigation in order to establish the relation between the enhanced activity and the composition of the catalyst.

The results of the activity–composition study are shown in Fig. 1 (see Table 1*A*, Runs 6, 7, 25, 26, 22, 11, 12, 15, 16, 23, 18AB, 20, and 14). There is a region of enhanced activity for mixtures containing relatively small amounts of chromium oxide. The values for the 13% chromium oxide catalyst were obtained in tests where the space velocity was varied, and within the limits investigated, the activity is independent of such variations. The two results for the 100% chromium oxide catalyst were obtained with oxide prepared by different methods. The smaller of the two values found for the 45% chromium oxide catalyst was obtained when the catalyst was not exposed to the standard pre-treatment with hydrogen. The nature of the curve is indicative of a promoter action in the mixed catalyst, rather than simple compound formation, or mechanical mixture behaviour (Griffith, " Contact Catalysis," Oxford University

FIG. 1.

Activity–composition relationship for the mixed catalyst, chromium oxide–activated alumina in the benzonitrile–butadiene cyclisation at 400° C.

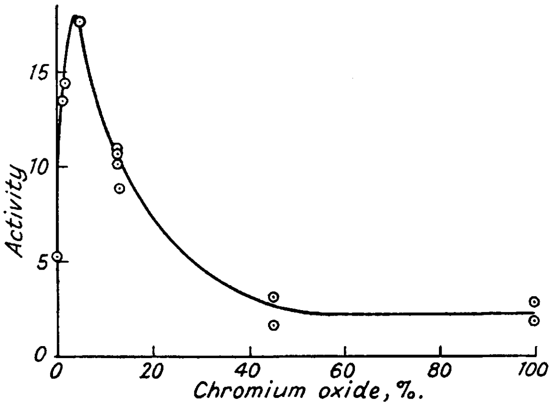


TABLE I.

Summary of data and results.

Run.	Catalyst.	T (°c.).	Space velocity, l./hr./c.c.	Ratio (mol.) $\frac{R{\cdot}CN}{C_4H_6}$.	C_4H_6 input (mols./hr.).	Pyridinic product (mols. $\times 10^{-4}$).	C_4H_6 (mols. %) conversion to pyridinic product.	Space-time yield mols. $\times 10^{-4}$/hr./100 c.c. catalyst).	Activity of catalyst.	Duration of test (hrs.).
(*A*) Benzonitrile and butadiene: 2-phenylpyridine.										
6	—	393	0·531	3·0	0·083	0·60	$0{\cdot}02_4$	1·45	—	3·0
7	Z–1	396	0·525	2·5	0·093	3·09	$0{\cdot}11_2$	7·38	5·08	3·0
10	Z–2	398	0·272	2·3	0·048	2·12	$0{\cdot}14_7$	5·45	3·76	6·0
13	Z–3	398	0·418	3·3	0·056	1·10	$0{\cdot}06_3$	2·77	1·91	3·0
8	Z–4	396	0·482	2·8	0·086	2·32	$0{\cdot}09_0$	5·16	3·55	3·0
11	Z–5*a*	397	0·288	2·4	0·047	12·0	$0{\cdot}42_6$	16·0	11·0	6·0
16	Z–5*a*	402	0·049	3·0	0·160	167	2·85	15·7	10·8	3·66
21	Z–6	400	0·241	4·7	0·120	12·3	0·53	10·1	6·96	1·92
14	Z–7*a*	393	0·323	3·2	0·048	1·17	0·81	2·77	1·91	3·0
22	Z–5*b*	400	0·234	2·9	0·107	30·9	$0{\cdot}96_3$	25·8	17·8	3·0
25	Z–5*c*	400	0·265	3·1	0·074	15·5	$0{\cdot}69_6$	20·1	13·8	3·0
26	Z–5*d*	400	0·265	2·6	0·106	20·1	$0{\cdot}65_4$	21·0	14·5	3·0
12	Z–5*a*	400	0·055	3·2	0·046	34·8	2·53	14·9	10·3	3·0
15	Z–5*a*	398	0·307	2·6	0·054	5·22	$0{\cdot}33_4$	12·9	8·90	3·0
23	Z–5*e*	396	0·311	2·3	0·112	4·68	0·14	5·12	3·53	3·0
18AB	Z–5*e*	398	0·262	3·3	0·149	4·50	0·10	2·64	1·82	3·0
20	Z–7*b*	400	0·538	4·1	0·108	3·09	$0{\cdot}09_6$	4·52	3·11	2·0
17AB	Z–5*a*	475	0·233	3·1	0·189	135	2·50	6·29	43·4	2·75
19AB	Z–5*e*	475	0·255	3·2	0·151	12·4	0·36	9·68	6·68	2·75
(*B*) Acetonitrile and butadiene: 2-methylpyridine.										
8	—	395	0·342	2·8	0·056	1·30	$0{\cdot}04_6$	1·88	—	5·0
12	Z–1	400	0·264	2·9	0·043	7·00	0·32	10·0	5·32	5·0
13	Z–5*a*	398	0·286	3·2	0·038	5·85	0·51	15·6	8·29	3·0
15	Z–1	301	0·062	2·5	0·051	1·62	0·10	0·63	0·34	3·0
14	Z–5*a*	300	0·062	3·6	0·052	1·62	0·10	0·63	0·34	3·0
16AB	Z–5*a*	475	0·346	3·0	0·176	115	0·98	38·2	20·31	3·0
9	Z–1	398	0·048	3·2	0·043	27·0	1·26	6·30	3·55	5·0
(*C*) Hydrogen cyanide and butadiene: pyridine.										
6	—	404	0·278	3·6	0·215	2·41	0·11	3·0	—	1·0
7	Z–5*a*	404	0·284	3·1	0·096	9·78	0·37	11·4	3·80	2·75
(*D*) Cyanogen and butadiene: 2-cyanopyridine.										
2	—	400	0·307	3·0	0·047	11·5	0·49	16·7	—	5·0
3	Z–5*a*	400	0·253	3·0	0·040	62·3	5·22	149	8·92	3·0

TABLE II.

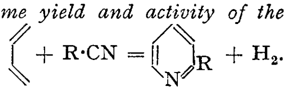
Summary of material and nitrile recoveries.

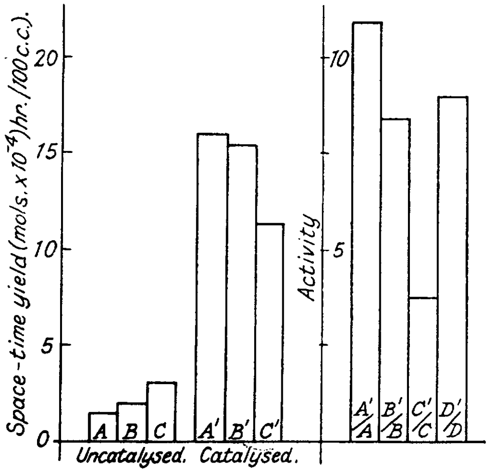
Run.	Catalyst.	*T* (° c.).	Material recovery (total), % of input.	Combined-nitrogen recovery (total), %.	Conversion of nitrile, % of input.	Pyridinic product yield, calc. on nitrile converted, %.
(*A*) Benzonitrile and butadiene : 2-phenylpyridine.						
22	Z-5*b*	400	99·0	98·7	4·3	8·0
11	Z-5*a*	400	97·2	100	3·7	4·8
17	Z-5*a*	475	96·0	97·2	5·5	14·1
(*B*) Acetonitrile and butadiene : 2-methylpyridine.						
13	Z-5*a*	400	95·5	93·5	19·5	0·83
(*C*) Hydrogen cyanide and butadiene : pyridine.						
7	Z-5*a*	400	80·3	78·0	22·7	0·53
(*D*) Cyanogen and butadiene : 2-cyanopyridine.						
3	Z-5*a*	400	81·3	—	22·3	8·5

Press, 1948). It is significant that Eischens and Selwood (*J. Amer. Chem. Soc.*, 1947, **69**, 1590) found that the magnetic susceptibility of chromium oxide on alumina decreases with increasing concentration of chromium oxide, but in the region of low chromium oxide compositions it is much larger than for the higher concentrations. The region of low chromium oxide compositions is the region where the enhanced catalytic activity was observed, and it would seem that the activated alumina serves the two-fold purpose of maintaining and increasing the extent of the chromium oxide surface and of providing a surface of chromium oxide of proper nature for catalytic activity. Both the reactants are unsaturated and are probably sensitive to the nature of the metallic oxide surface. As to the actual mode of action of these catalysts there is very little information. Rideal and Herington (*loc. cit.*) in cyclisation studies using a MoO_2-activated alumina catalyst and hydrocarbons, attributed the activity of the MoO_2 to the presence of two unpaired electrons in the ion.

FIG. 2.

Comparison of space-time yield and activity of the catalyst in the reaction :





In A, A' . . ., R = C_6H_5 ; *in B, B'* . . ., R = CH_3 ; *in C, C'* . . ., R = H ; *in D, D'* . . ., R = CN.

In Fig. 2 a comparison is made of the results for the uncatalysed and the catalysed reaction when cyanogen, hydrogen cyanide, acetonitrile, and benzonitrile are used in turn with butadiene (see Table I*A*, 6, 11; Table I*B*, 8, 13; Table I*C*, 6, 7; Table I*D*, 2, 3). On comparison with the results of the uncatalysed study, it is seen that the space-time yield has in each case been markedly increased, and also that the trend, except with cyanogen, is now the reverse of that formerly observed. Considering the activity of the catalyst, one finds that it decreases in the order R = phenyl, methyl, hydrogen. Although the phenomenon undoubtedly involves other factors as well, it would seem that the polarisation of the nitrile group at the catalyst surface is an important factor in the mechanism of the reaction, for the above sequence is also the order in which the polarizability of the cyano-group varies for these nitriles, *i.e.*, greatest for benzonitrile and least for hydrogen cyanide. The order of the catalytic effect in the cyanogen–butadiene reaction is difficult to interpret because there are two potential reaction centres per molecule of nitrile. It is seen, however, that it lies below the value for the benzonitrile–butadiene reaction, and this is in accord with the above discussion. Studies of this cyclisation with dienes other than butadiene are in progress in order to obtain further information on this question.

The effect of temperature on the rate of the catalysed reaction is seen on comparison of some of the data in Table I (*i.e.*, 1*A*, 11, 17AB, 18AB, 19AB, 1*B*, 15, 12, 14, 13, 16AB). When using activated alumina only, or the chromium oxide-activated alumina mixture, it was found that the reaction occurred appreciably at temperatures as low as 300°, and that the rate was markedly accelerated at 475°. It should be noted that the activity figures at these temperatures are only qualitative since they have been calculated with the uncatalysed results at 400° as the standard of reference. At 300°, catalytic activity being judged this way, it is seen that the mixed catalyst has the same activity as the alumina by itself.

The poisoning of the catalysts has not been studied, but their activity decreased with reaction time, more so at the higher temperatures than at 400°. For this reason the duration of the runs in the activity studies was standardised to about **3** hours. The catalysts could be revived by oxidation and hydrogen pre-treatment in the usual manner.

EXPERIMENTAL.

Preparation of Catalysts.—*Z*-1. A commercial grade of activated alumina (Messrs. Peter Spence & Sons Ltd.), 8—16 mesh, was used. A slow stream of air was passed over the catalyst at the reaction temperature, followed by a nitrogen flush, before each test.

Z-2. The catalyst was prepared essentially as described by Kline and Turkevich (*loc. cit.*). A solution of nickel nitrate, sufficient to give about 10% of nickel, was evaporated on the alumina. The nitrate was then decomposed at 300—400°, and the mixture heated in air at 300°. The catalyst was finally flushed with nitrogen and reduced with hydrogen, also at 300°, for approximately one hour.

Z-3. A paste of phosphoric acid (306 g.; *d* 1·75) and kieselguhr (108 g.) was heated at about 450—500° until a cement had formed. This was powdered to 8—16 mesh for the tests.

Z-4. A mixture of activated alumina (100 g.) and phosphoric acid (100 g.; *d* 1·75) was heated at 400—450° for several hours. It was crushed to 8—16 mesh before use.

Z-5 *a, b, c, d, e*. Samples *a*, *b*, *c*, and *d* were prepared essentially as described by Kline and Turkevich. A sufficient amount of ammonium dichromate in solution was mixed with activated alumina to give on evaporation the required weight of chromium oxide, calculated as Cr_2O_3. The dichromate was decomposed by slowly introducing the mixture into a furnace at 400—475°. The catalyst was then heated for about 2 hours in a stream of air at this temperature. It was flushed with nitrogen and reduced with hydrogen at 450—475° for one hour. Analysis for chromium gave the compositions for *a*, *b*, *c*, and *d* as 12·8, 4·5, 1·0, and 2·0% of chromium oxide respectively. Catalyst 5*e* containing 45% chromium oxide was compounded by Imperial Chemical Industries Limited.

Z-6. A mixture of magnetic iron oxide, Fe_3O_4 (B.D.H.), and activated alumina was prepared to contain 10% of iron oxide, and compounded to pellets suitable for the activity tests.

Z-7 *a*, *b*. Catalyst 7*a* was prepared by thermal decomposition of ammonium dichromate, followed by the oxidation–reduction treatment as for the mixed catalysts. It was difficult to pellet and not very satisfactory for tests. Catalyst 7*b* was prepared by reduction of chromic acid in aqueous-alcoholic solution as described by Turkevich, Fehrer, and Taylor (*J. Amer. Chem. Soc.*, 1941, **63**, 1129). After being dried in an oven, it was activated by the air–nitrogen–hydrogen treatment as for the Z-5 catalysts, at 450°. It was crushed to 8—16 mesh before use.

Materials, Apparatus, and Analysis of Products.—These were essentially the same as described in Part I. A known volume of catalyst was used in each case, and the results were subsequently calculated to a standard volume to obtain comparable space-time yields and activities. The data and results are summarised in Tables I and II.

For the nitrogen analysis, the normal Kjeldahl digestion was abandoned in favour of digestion in sealed tubes, in order to avoid losses by volatilisation. About 0·5 g. of the sample was weighed in a Pyrex tube, covered with 10 c.c. of concentrated sulphuric acid and sealed off. The tube was then heated for 15—20 hours at 100—120° in the case of acetonitrile, and 150—175° in that of benzonitrile. The accuracy was within 1%.

In the presence of the catalyst the conversion of the nitrile into ammonia and related products was considerably greater than that observed in the uncatalysed reactions. The material and nitrogen balances listed in Table II are typical of the results found. The nitrile conversions as listed here include also the nitrile lost in experimental procedure, and the yields calculated on these conversions can therefore be improved if these losses can be further decreased. The total material recovery figures indicate that some of the loss is incurred over the catalyst bed, owing probably to carbonaceous products being formed and deposited on the bed, and to pyrolysis to gaseous products such as methane, ethylene, and nitrogen. This aspect of the work has not yet been followed further.

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