p-Dibromobenzene and Cyclopentadienylsodium.—Cyclopentadienylsodium was prepared from cyclopentadiene (33 g.) by the method used in the preceding experiment. p-Dibromobenzene (59 g.) and xylene (300 cc.) were added at the boiling point of the liquid ammonia. The ammonia was allowed to distil off overnight. The next day liquid ammonia (500 g.) and sodium (11.5 g.) again were added. One hour later ferrous chloride (45 g.) was added. After standing at room temperature for several days the xylene solution was distilled. Dicyclopentadienyliron (10 g.) was obtained first. The fraction distilling from 230–240° (33 mm.) (15 g.) was crystallized from alcohol and cyclopentadienyl-(phenylcyclopentadienyl)-iron identical with that obtained from dicyclopentadienyliron and diazotized aniline was obtained.

Anal. Calcd. for $C_{16}H_{14}Fe$: C, 73.2; H, 5.34; Fe, 21.35; mol. wt., 262. Found: C, 73.5; H, 5.32; Fe, 21.3; mol. wt., 250.

The data in Table II give the absorption maxima in mμ and the corresponding extinction coefficients. The maxima in parentheses are either shoulders or buried peaks. The others are clear maxima. Blank spaces indicate either that the spectra did not cover these regions or that no definite conclusions could be drawn from the curves.

The spectra were obtained with a Cary recording spectrophotometer model 11.

Acknowledgment.—The writer is indebted to Dr. C. J. Pedersen who collected and calculated the ultraviolet and visible spectra.

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[CONTRIBUTION FROM THE WALKER LABORATORY, DEPARTMENT OF CHEMISTRY, RENSSELAER POLYTECHNIC INSTITUTE]

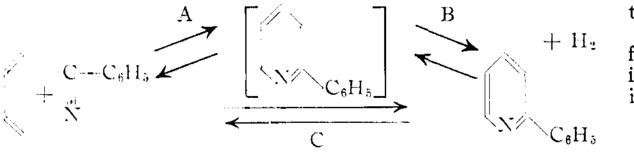
The Reaction of Cyanogen and Related Nitriles with 1,3-Dienes. VIII. Catalyst Evaluations[1]

BY GEORGE J. JANZ AND WILLIAM J. H. McCULLOCH[2]

RECEIVED DECEMBER 1, 1954

The activity of Al_2O_3 in the nitriles–dienes cyclization–dehydrogenation reaction at 400° is investigated. The thermal stabilities of benzonitrile and related nitriles and heptane over Al_2O_3 at 400° also have been examined to gain information on the mechanism of the reaction on this surface. The activity of the alumina in promoting the rate of the nitriles–dienes cyclization is best understood as another example of the general acid catalysis of diene addition reactions.

The synthesis of phenylpyridine by the reaction of benzonitrile with butadiene at 400° is an example of a more general reaction for the formation of pyridinic products from nitriles and dienes. In a previous communication[3] the thermodynamic aspects of the two step process, and the over-all reaction



have been considered, and the results for fifteen different catalysts described. In the temperature range of 400°, the free energy changes for the cyclization (A) and dehydrogenation (B) steps are +23 and −27 kcal./mole, respectively. The overall process (C) is thermodynamically favored because of the very large negative ΔF for the second step. Accordingly, catalysts which promote the high temperature Diels–Alder cyclization step (A) are of direct interest for the catalytic synthesis of pyridines from nitriles and dienes. In present work, the catalyst tests[3] are extended to an investigation of the activity of Al_2O_3 in the nitriles–dienes cyclization–dehydrogenation reaction at 400°. The benzonitrile–butadiene reaction, with 2-phenylpyridine as product, again was selected as the test reaction because of the high thermal stability of this nitrile. The thermal stabilities of related nitriles and heptane over Al_2O_3 also have been examined to gain information on the mechanism of the reaction on this surface.

Experimental

The benzonitrile (Eastman Organic Chemicals practical grade) was dried over P_2O_5 and distilled at 50 mm. pressure before use. The butadiene (Matheson Co. Inc.) was a C.P. grade of a purity not less than 99%. It was passed through drierite and distilled once before use.

Catalysts.—All catalysts were prepared in 1/8 inch pellet form by Harshaw Chemical Co. for this work. The following were the specifications in the five catalysts used in this investigation:

Code	Type	Composition
A-1	Al_2O_3	99% Al_2O_3, 0.5% Na_2O, 0.03% SiO_2, 0.03% Fe_2O_3
A-2	Al_2O_3	93% Al_2O_3 . . . 6.0% SiO_2, 0.5% CaO
A-3	Al_2O_3	100% Al_2O_3
C-1	Cr_2O_3–Al_2O_3	4% Cr_2O_3, 96% Al_2O_3 (type A-1)
C-2	Cr_2O_3–Al_2O_3	4% Cr_2O_3, 96% Al_2O_3 (type A-3)

Each catalyst was preheated as described in the previous work.[3] In addition the pure alumina catalysts were heated at 500° and about 10^{-4} mm. pressure for 24 hr. and flushed with nitrogen before each experiment.

Apparatus and Procedure.—The apparatus and procedure for the catalyst activity tests have been described elsewhere[3] in detail. The relative surface areas were determined by a modified form of the B.E.T. apparatus as described by Barr and Anhorn.[4] The catalyst samples were degassed at 350°, before the surface areas were measured, for 12 hours using a mercury diffusion pump.

Phenylpyridine Reaction.—The experimental conditions for the benzonitrile–butadiene cyclization-dehydrogenation tests and the yields are summarized in Table I. Each run was 2 hours long and the temperature is a weighted average observed for the catalyst during this period. The reaction mixture, an equimolar mixture of butadiene, benzonitrile and nitrogen, was metered at controlled rates to give approximately a 4-second reaction time in each case (Table I). The total material balance shows, within experimental error, a satisfactory account for the total input as crude

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(1) Abstracted in part from the thesis submitted by W. J. G. McCulloch in partial fulfillment of the requirements for the degree of Doctor of Philosophy (Chemistry), Rensselaer Polytechnic Institute, Troy, N. Y.

(2) Research Corporation Fellow in Chemistry, 1951–1953.

(3) G. J. Janz, W. J. G. McCulloch and E. F. Timpane, *Ind. Eng. Chem.*, **45**, 1343 (1953).

(4) W. E. Barr and V. J. Anhorn, "Scientific Glass Blowing," Instruments Publ. Co., Pittsburgh, Pa., 1949, p. 273.

liquid product and catalyst deposits. The latter, measured as a gain in weight of the bed, amounted to about 2–5 wt. per cent. of the input in each case. The benzonitrile recovery was determined by distillation at 50 mm. pressure with a semi-micro concentric glass tube Podbielniak analyzer. The amount of phenylpyridine was measured by non-aqueous titration technique, using perchloric acid in glacial acetic acid.[5a,b] The space–time yield, which is in first approximation proportional to the rate of reaction, was calculated with reference to an arbitrary reference volume of catalyst. Comparison of the space–time yields rather than the use of the standard reference curve[3] is recommended to estimate relative activities owing to the different nature and surface areas of these specimens. The surface areas for catalysts A-1, A-2, A-3, C-1, C-2, before an experiment, and A-3 after an experiment are reported in Table II (no. 1, 2, 3, 10, 11 and 6, respectively).

TABLE I

EXPERIMENTAL CONDITIONS AND YIELDS

Run	Catalyst		Experimental conditions				Phenylpyridine	
	Type	Cc.	Temp., °C.	Time, sec.	Material balance, wt. %	Conversion per pass mole %	Yield,[a] mole %	Space–time yield[b] (× 10^4)
1	A-1	85	402	4.0	104	7.3	11	24
2	A-2	78	422	4.0	102	7.8	47	130
3	A-3	85	402	4.4	104	13.6	24	99
4	C-1	32	414	4.3	100	4.7	16	39
5	C-2	32	404	3.8	100	11.0	19	117

[a] Calculated on the benzonitrile converted per pass. [b] In units of moles/hr./100 cc.

Thermal Stabilities.—The thermal stability of each reactant and some related nitriles, and the changes in the surface area of the pure alumina catalyst (A-3) caused by these, were measured. The nitrile or diene, in equimolar mixture with nitrogen, was metered to the catalyst bed to give a contact time of 3.5 to 4.5 seconds, the duration of each test being two hours. The thermal stabilities[6] under these conditions for benzonitrile, acetonitrile and propionitrile, were found to be 92, 82 and 85%, respectively. With propionitrile some cracking to acetonitrile was observed. For butadiene, 47% was recovered unchanged, the remainder being accounted for as catalyst deposit and polymerized products. Acrylonitrile also was observed to have a low thermal stability on this surface. Only 32% was recovered unchanged after a 4-sec. pass at 400°. Some propionitrile was formed in this case in addition to high boiling fractions. When a mixture of benzonitrile and butadiene was passed over the catalyst (Table I, run 3), the nitrile and diene conversions were only 14 and 18%, respectively, in contrast to 8 and 53% when these reactants were used singly. The gain in weight, ΔW, of 100 cc. of catalyst, the maximum temperature rise, ΔT, and the surface areas, are summarized in Table II.

TABLE II

SURFACE AREAS OF CATALYSTS

No.	Type	Catalyst treatment	ΔW,[a] g.	ΔT,[b] °C.	B.E.T. surface area, m.^{2}/g.
1	A-1	Oxidized and reduced, 450°	..	..	89.1
2	A-2	Same	..	..	249
3	A-3	Same	..	..	194
4	A-3	Benzonitrile, 2 hr., 400°	3.1	16	188
5	A-3	Butadiene, 2 hr., 400°	11.6	79	166
6	A-3	Benzonitrile and butadiene, 2 hr., 400°	3.6	30	177
7	A-3	Acetonitrile, 2 hr., 400°	3.1	13	182
8	A-3	Propionitrile, 2 hr., 400°	2.7	11	194
9	A-3	Acrylonitrile, 2 hr., 400°	14.1	46	150
10	C-1	Oxidized and reduced, 450°	..	..	75.6
11	C-2	Same	..	..	181

[a] Gain in weight of the catalyst bed (100 g.) after a 2-hour experiment. [b] Temperature increase of catalyst bed observed during the experiment.

Heptane.—Three experiments were carried out to test the activity of the pure alumina (A-3) and the chromia–alumina (C-2) for the aromatization of *n*-heptane to toluene. At 480° and a 20-sec. contact time it was found that products containing approximately 2 and 22% toluene were obtained when *n*-heptane was passed over the catalysts (A-3) and (C-2), respectively. At 400° and 4 sec. contact times, no toluene was formed when either the pure alumina (A-3) or the chromia–alumina (C-2) were used. Under conditions comparable to the phenylpyridine reaction, no conversion to toluene was observed.

Discussion

The data (Table I) established that the nitriles–dienes cyclization–dehydrogenation reaction rate is primarily catalyzed by a pure alumina oxide surface, although the chromia–alumina surfaces have a slightly more beneficial effect. This is more clearly seen from a comparison of the ratio of the space–time yields, using the low surface area alumina as reference standard.

Catalysts ratio	A-2/A-1	A-3/A-1	C-1/A-1	C-2/A-1	C-2/A-3
Space–time, yields	5.4	4.1	1.6	4.9	1.2
Surface areas	2.8	2.1	0.86	2.0	0.97

Thus the catalytic activity in this reaction of the two high surface area aluminas is the same order of magnitude and much greater than the increase in surface area. Calculating the space–time yields per square meter of surface for the three aluminas, A-1, A-2, A-3, the results are 0.26, 0.53 and 0.53, respectively. It follows that the purest alumina (A-3) and the alumina having 6% SiO_2 (A-2) have quite comparable catalytic effects and are almost twice as active as the alumina having 0.5% Na_2O.

Inspection of the data for the chromia–alumina catalysts (Table I) shows that, referred to the low surface area alumina as standard, the chromia on the surface area alumina (C-2) has an "apparent" activity 4.9 times greater than the standard. Referring the space–time yields for these two runs to the data for the pure alumina used as the chromium oxide support in each case, shows that the activities of the two chromia–aluminas are in each case only 1.6 and 1.2 times greater than the respective pure aluminas. Thus some enhancement in the reaction rate can be attributed to the chromium oxide, but the greatest portion must be due to the activity of the new catalyst support. By contrast, no appreciable aromatization of *n*-heptane was observed on the alumina at 400° and 475°, whereas the chromia–alumina surface (C-2) did catalyze the aromatization process at 475°. A characteristic of the process involved in the ring closure of paraffin and olefin hydrocarbons is that they are all processes of dehydrogenation.[7–11] The nitriles–dienes system is more complex, involving two reactant species, but the formation of the pyridinic product is a consequence of a cyclization–dehydrogenation type reaction, *i.e.*

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(5) (a) G. J. Janz and N. E. Duncan, THIS JOURNAL, **75**, 5389 (1953); (b) J. F. Fritz, *Anal. Chem.*, **22**, 1028 (1950).

(6) Defined as weight per cent. of reactant recovered unchanged after one pass through the catalyst bed.

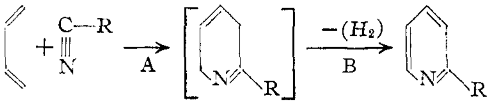
(7) H. Hoog, J. Verheus and F. J. Zuiderweg, *Trans. Faraday Soc.*, **35**, 993 (1939).

(8) R. C. Pitkethly and H. Steiner, *ibid.*, **35**, 979 (1939).

(9) G. H. Twigg, *ibid.*, **35**, 1006 (1939).

(10) H. S. Taylor and H. Fehrer, THIS JOURNAL, **63**, 1387 (1941).

(11) H. Steiner, *ibid.*, **67**, 2052 (1945).



The dihydro-cyclic intermediate has never been isolated, the loss of hydrogen being a spontaneous process under the reaction conditions. The beneficial effect of the aromatization-type catalysts reported in the earlier work,[3] and observed again in the present study, undoubtedly can be attributed to promotion of the dehydrogenation step (B) in the over-all process.

The mode of action of the alumina itself must be basically different from the aromatization catalysts. Aluminum oxide is known to be an amphoteric substance, having the properties of an acid or base depending on its environment. Under the condition of the present work (400–500°) the structure is predominantly the γ-alumina structure. The properties of the silica–alumina cracking catalysts have been interpreted on a chemical basis to the existence of aluminum ions (γ-alumina) with the characteristic of a Lewis acid.[12] The surface is active to electron donors from the gas phase to form complexes with the Lewis acid. In the present work, the cracking of propionitrile over pure alumina (A-3), and the lower catalytic activity of the alumina containing the basic oxide rather than the acidic oxide (*i.e.*, A-1 and A-2, respectively) are in accord with some acidic properties of this surface. Comparison of the relative surface areas when nitriles alone, and butadiene, were passed over the pure alumina (Table II, no. 1, 7, 8 and 5, respectively) indicates that the decrease in area is much smaller for the nitriles than the dienes (*i.e.*, the $C{\equiv}N$ and $CH{=}CH_2$) groups. This and the temperature rise indicate a more selective adsorption of the olefinic group. The data for acrylonitrile are interpreted as reaction through the olefinic group, the polar nature of the nitrile group promoting the double bond to a more reactive state.

The formation of some ammonium carbonate in the pyrolyses of the nitriles over pure alumina, and reported as a by-product in the nitriles–dienes reaction[3,13,14] can be attributed to a secondary reaction occurring in the alumina surface. The γ-alumina structure is formed from boehmite by dehydration at temperatures above 350°. The water thus expelled hydrolyzes the nitrile in these systems leading to the ultimate formation of ammoniacal products. Preliminary work in this Laboratory indicated that this reaction can be minimized by exhaustive high vacuum drying of the alumina at 500° prior to use in the nitriles–dienes reaction.

The preferential formation of certain isomers[13,14] and the enhanced rates in the heterogeneous reactions have been interpreted[13] in the light of a Diels–Alder reaction mechanism. Wassermann and coworkers[15] have reported that the Diels–Alder type reaction is susceptible to a general acid catalysis. In the present work, the activity of the alumina in promoting the rate of the nitriles–dienes cyclization is best understood as another example of the general acid catalysis of diene addition reactions.

Acknowledgment.—The authors wish to thank Miss Sonja Krause of this Laboratory for the measurements of surface areas. This work was made possible by grants-in-aid from Research Corporation of New York and the Research Grants Committee of Rensselaer Polytechnic Institute.

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[12] A. G. Oblad, T. H. Milliken and G. A. Mills, "Advances in Catalysis," Vol. IV, Academic Press, Inc., New York, N. Y., 1952, p. 231.

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TROY, N. Y.

[CONTRIBUTION FROM THE RESEARCH LABORATORIES, TENNESSEE EASTMAN CO., DIVISION OF EASTMAN KODAK CO.]

Sulfur-containing Pivalic Acid Derivatives. I. Sulfonyldipivalic Acid

BY JOSEPH L. GREENE, JR.,[1] AND HUGH J. HAGEMEYER, JR.[2]

RECEIVED DECEMBER 15, 1954

Bromopivalic acid was synthesized from hydroxypivalic acid. The synthesis of thiodipivalic acid in excellent yields was accomplished by the reaction of bromopivalic acid with sodium sulfide; the ease with which this neopentyl halide is converted without rearrangement is unusual. Oxidation of thiodipivalic acid with hydrogen peroxide led to sulfonyldipivalic acid. A number of new sulfur-containing pivalic acid derivatives were synthesized. The preparation and properties of these compounds are described.

The literature contains relatively few references to aliphatic sulfonyldicarboxylic acids. The first member of the series, sulfonyldiacetic acid, also was the first prepared.[3]

It has been shown that α-sulfonylcarboxylic acids are analogous to α-keto acids in that they are decarboxylated readily by heat.[4] A general discussion of acids having the type formula $HOOCCHR{-}SO_2CHRCOOH$ has been published.[5] Since the advent of nylon, dicarboxylic acids have been of growing general interest as intermediates for polyamides and other condensation polymers. Since sulfonyldipivalic acid contains neither an α-sulfonyl group nor an α-hydrogen atom, it is thermally very stable, being unaffected by heating for 4 hours at a temperature 30° above its melting point. Hence it is of interest as an intermediate in the preparation of polyesters, polyamides, plasticizers, and other useful products.

The purpose of this paper is to describe the pro-

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[1] Chemistry Department, Emory University, Emory University, Georgia.

[2] Texas Eastman Company, Longview, Texas.

[3] J. M. Loven, *Ber.*, **17**, 2817 (1884).

[4] R. Otto, *ibid.*, **21**, 89 (1888); R. Otto and W. Otto, *ibid.*, **21**, 992 (1888).

[5] J. M. Loven and R. Ahlberg, *ibid.*, **54B**, 227 (1921).