TABLE I

Substrate	Ratio, moles substrate/ $K_3[Co(CN)_5]$	Mole % H_2 absorbed[a]	Initial rate of H_2 absorp. (ml./min.)	Products
Isoprene	6.7	79	12	~85% 1,4-, ~15% 1,2-addition
1,3-Cyclohexadiene	7.0	96	60	Cyclohexene
Styrene	2.9	89	21	Ethylbenzene
Tiglic aldehyde	3.4	57	22	α-Methylbutyraldehyde
Methacrylic acid[b]	3.3	97	35	Isobutyric acid
Sorbic acid[c]	3.3	87	57	2-Hexenoic acid
Cinnamic acid[c]	3.3	49	8	β-Phenylpropionic acid
Methyl methacrylate	3.1	84	4-24	Methyl isobutyrate, isobutyric acid
Benzil[c]	1.7	88	..	Benzoin
Cyclohexene oxide	3.3	45	9	Cyclohexanol
Styrene oxide	2.9	53	4	β-Phenylethanol
Azoxybenzene	1.7	68	..	Azobenzene

[a] Based on 1 mole H_2/mole substrate; does not include hydrogen absorbed by catalyst.   [b] Added as the sodium salt. [c] An equivalent of potassium hydroxide also was added.

rated acids (as salt or ester) and aldehydes, 1,2-diketones, epoxides and azoxy compounds.

Hydrogenations generally were carried out using a cyanide/cobalt ratio of 5.1 at a cobalt concentration of 0.15 M although other ratios and concentrations also were effective. The reductions described here were carried out at room temperature and a hydrogen pressure of one atmosphere; the extent and rate of the reaction were followed by measurement of hydrogen absorption. Water-insoluble substrates were added either directly or, prior to addition, were dissolved in a non-polar solvent such as benzene.

The catalyst was not only specific with respect to the type of functional group reduced, but also was sensitive to other structural features of the substrate molecule. For example, styrene and α-methylstyrene were reduced readily while 1,1-diphenylethylene, indene, and propenylbenzene were not; acrylic acid was reduced only at elevated temperatures, while acrylic acids substituted in the α-position by C_6H_5, CH_3 or $HOOCCH_2$ groups were reduced at room temperature.

Propionaldehyde yielded the dimeric aldehyde, α-methylvaleraldehyde, evidently via a base-catalyzed aldol condensation. Cinnamaldehyde yielded the aldol condensation product of β-phenylpropionaldehyde, 2-benzyl-5-phenylpent-2-enal.

It is of interest that certain substrates such as nitrobenzene and benzoquinone were not reduced catalytically unless added to the prehydrogenated catalyst in less than stoichiometric quantities. After this quantity had been reduced, further "incremental additions" could be made until the molar quantity of substrate which was reduced exceeded that of the cobalt present in the catalyst system. Thus, the catalytic hydrogenation of these compounds and regeneration of the catalyst were demonstrated. Azobenzene and hydroquinone were formed, respectively. Allyl chloride or allyl acetate yielded propylene rapidly in good yield. Hydrogen peroxide and certain inorganic salts also have been reduced.

1,114,183 concerning the reduction of butadiene to butene by pentacyanocobaltate(II) has been issued to Imperial Chemical Industries.

No other homogeneous hydrogenation system[5] is known to reduce such a wide variety of substrates catalytically under such mild conditions. A more detailed description of this work, as well as observations on the course of the reductions, will be made at a future date.

(5) For a review of such systems, see J. Halpern in Advances in Catalysis, 11, 303 (1959), and J. Halpern, J. F. Harrod and B. R. James, J. Am. Chem. Soc., 83, 753 (1961).

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MACRORETICULAR ION EXCHANGE RESINS

Sir:

A new polymerization technique has been discovered that yields a cross-linked ion exchange structure entirely different from the conventional homogeneous gels and having a truly macro-porous structure similar to those of conventional adsorbents such as alumina and bone char. The polymerization technique involves the suspension polymerization of styrene–divinylbenzene copolymers in the presence of a substance that is a good solvent for the monomer but a poor swelling agent for the polymer. These polymers have been converted to a sulfonic acid cation exchanger (Amberlyst 15) by conventional sulfonation techniques and to a quaternary ammonium anion exchanger (Amberlyst XN-1001) by chloromethylation followed by amination with trimethylamine.

The pore properties of the dry macroreticular ion exchange resins were studied by means of nitrogen adsorption at −195° and by measurement of the true density (helium displacement) and apparent density (mercury displacement). A summary of these measurements is given in Table I along with comparison data for Amberlite IR-120 and Amberlite IRA-400, conventional sulfonic acid cation and quaternary ammonium anion exchange resins, respectively. It is quite evident that any pore structure that exists in the conventional resin gel structure disappears on drying

TABLE I

COMPARISON OF PHYSICAL PROPERTIES OF CONVENTIONAL AND MACRORETICULAR ION EXCHANGE RESINS

Resin	Form	Moisture holding capacity, % H_2O	Surface area, sq. meters/g. of dry resin	Apparent density,[a] g./ml.	True skeletal density,[b] g./ml.	Porosity (P), ml./ml.	Av. pore diam., Å.
Amberlyst 15	Na+	50	42.5	1.012	1.513	0.319	288
Amberlite IR-120	Na+	46	<0.1	1.489	1.518	.018	
Amberlyst XN-1001	Cl⁻	60	62.9	0.559	1.136	.508	645
Amberlite IRA-400	Cl⁻	45	<0.1	1.136	1.140	.004	

[a] Mercury displacement. [b] Helium displacement.

as a result of a collapse of the gel structure. The macroreticular resins, on the other hand, possess a non-gel pore structure that does not collapse on drying. Electron microscopic examination of ground, dry samples reveals no internal pore structure for the conventional resin and a definite pore structure for the macroreticular resins.
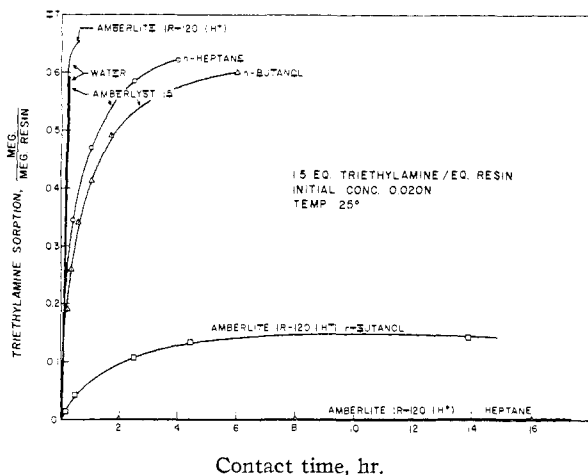

Contact time, hr.

Fig. 1.—Rates of sorption of triethylamine by Amberlyst 15 and a conventional resin in various solvents.

The exchange kinetics of the Amberlyst 15 were compared with the conventional Amberlite IR-120 by studying the sorption of triethylamine from various solvents by the thoroughly dried hydrogen forms of the resin. The data (Fig. 1) show a remarkable difference in behavior between the two resins for solvents of low dielectric strength.

The difference between the macroreticular and conventional gel resins was noted further when the catalytic activities of the acid forms of Amberlyst 15 and Amberlite IR-120 were compared for the acid catalyzed decomposition of tert-butyl acetate into isobutylene and acetic acid at 25°. Thoroughly dried resins of the same particle size were compared. After 1 hour, the Amberlyst 15 activity was such that 80% of the equilibrium conversion was obtained and less than 1% was observed for the run with the Amberlite IR-120.

A similar catalytic study was conducted on the same resins for the reaction involving the synthesis of tert-butyl methacrylate from isobutylene and methacrylic acid at 0°. The two resins were compared by following the degree of conversion of the acid as a function of time. The data reveal the

same difference in catalytic activity as noted in the tert-butyl acetate reaction. With Amberlyst 15, 50% conversion was achieved in 4 hours and less than 1% conversion was noted with Amberlite IR-120 in the same time interval.

Detailed studies on the chemical, physical, and catalytic properties of these macroreticular ion exchange polymers are in progress.

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RECEIVED DECEMBER 20, 1961

HYDROGEN TRANSFER BETWEEN A PHENOL AND ITS PHENOXY RADICAL[1]

Sir:

The rate of transfer of an atom of hydrogen between a diamagnetic molecule RH and the paramagnetic radical R· may be determined either through measurements of the broadening of e.s.r. lines of R· or n.m.r. lines of RH. Preservation of the hyperfine structure of the e.s.r. spectrum of R· insures that the broadening of n.m.r. lines of nuclei in RH (except for the transferred hydrogen) yields a direct measure of the rate.[2] The condition is fulfilled for the transfer of hydrogen between 2,4,6-tri-tert-butylphenol and the corresponding phenoxy radical. The n.m.r. spectrum of a solution of the phenol in carbon tetrachloride consists of the expected four lines. The lines are about 0.4 cycle per second broad with no resolved spin–spin splittings. Addition of the phenoxy radical broadens all lines, the ring and butyl lines equally and the hydroxyl line less. With increasing temperature the ring and butyl lines become broader, while the hydroxyl line becomes narrower. The line of tetramethylsilane which had been added to the solution is also broadened as the concentration of radical is increased but always much less than the butyl or ring lines.

In the analysis of the data the effect of the non-specific dipolar broadening was allowed for, perhaps inaccurately, by subtraction of the breadth of the tetramethylsilane line. Since the correction is small compared with the large broadenings no great error is introduced into the over-all rates, but considerable uncertainty may be attached to the remarks in the final paragraphs concerning intermediate states.

(2) H. McConnell and S. Berger, J. Chem. Phys., 27, 230 (1957).