the methylene peak. Thermal reversion was observed by heating a degassed sample, originally containing 91% quadricyclene and 9% norbornadiene at 140° for 14 hours. At the end of that period the sample contained 56% quadricyclene and 44% diene. Vapor chromatography indicated the presence of no other products.

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CONTRIBUTION NO. 2744 FROM THE
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RECEIVED SEPTEMBER 1, 1961

SODIUM ZEOLITE ZK-4, A NEW SYNTHETIC CRYSTALLINE ALUMINOSILICATE

Sir:

One of the most interesting and useful of the purely synthetic zeolites is zeolite A.[1] This is one of the few zeolites whose lattice composition has thus far been found to be essentially constant with an SiO_2/AlO_2 molar ratio of 0.96 ± 0.05.[1,2] This apparent constancy of composition has been a matter of curiosity to some structural chemists interested in zeolites.

We recently synthesized a zeolite whose crystal structure is similar to, but whose chemical composition differs significantly from, zeolite A. Like zeolite A, the new compound (designated zeolite ZK-4) contains 24 tetrahedra in a cubic unit cell. The unit cell formula of sodium zeolite ZK-4 is $Na_9[(AlO_2)_9(SiO_2)_{15}]\cdot 27H_2O$ compared with $Na_{12}[(AlO_2)_{12}(SiO_2)_{12}]\cdot 27H_2O$ for sodium zeolite A. Because of the high SiO_2/AlO_2 ratio of zeolite ZK-4, a contraction of the unit cell compared with sodium zeolite A (a_0 = 12.32 Å.) is expected since the Si–O bond distance is shorter than the Al–O bond distance. X-Ray diffraction analysis disclosed a_0 = 12.16 ± 0.02 Å. for sodium zeolite ZK-4. By the method of Smith,[3] the unit cell of the new zeolite subsequently was calculated to be 1.33% smaller than that of sodium zeolite A or a_0 = 12.15 Å. A summary of pertinent X-ray diffraction data for sodium zeolite ZK-4 is presented in Table I.

Some of the molecular sieve properties of sodium zeolite ZK-4 are markedly different from those of sodium zeolite A as shown in Table II.

TABLE I

X-RAY DIFFRACTION DATA—SODIUM ZEOLITE ZK-4

(h,k,l)	d, Å.	I/I_{max}	(h,k,l)	d, Å.	I/I_{max}
100	12.07	100	600	2.033	4
110	8.57	71	621	1.904	2
111	7.025	50	541	1.881	1
210	5.422	23	622	1.835	1
220	4.275	11	630	1.813	1
300	4.062	48	444	1.751	1
311	3.662	59	632	1.737	1
320	3.390	33	710	1.718	4
321	3.244	64	641	1.669	4
410	2.950	60	721	1.653	1
411	2.862	14	722	1.611	1
420	2.727	8	730	1.595	1
421	2.661	4	650	1.558	1
332	2.593	13	652	1.510	1
422	2.481	2	811	1.501	1
430	2.435	1	821	1.465	1
511	2.341	2	653	1.450	1
521	2.225	2	831	1.415	1
440	2.162	2	751	1.405	1
441	2.120	1	654	1.385	1
530	2.080	1	744	1.349	1
531	2.061	1	910	1.345	1

TABLE II

ADSORPTIVE CAPACITIES OF ZEOLITES ZK-4 AND A AT ROOM TEMPERATURE

	G. sorbed/100 g. activated zeolite[a]			
	n-Hexane	n-Octane	3-Methylpentane	Water
NaA	0.4(20)	0.5(13)[1c]	0.3(20)	28.9(24)[1b]
CaA	12.6(20)	15.4(11)[1c]	.2(20)	30.5(24)[1b]
KA	0.2(20)	0 (11)[1c]	.2(20)	22.2(19)[1c]
NaZK-4	12.5(20)	12.6(11)	.2(20)	24.8(12)
KZK-4	0.4(20)	0.3(11)	.2(20)	19.5(12)

[a] Vapor pressure, mm., of adsorbate in equilibrium with adsorbent given in parentheses.

Of particular significance is the ability of sodium zeolite ZK-4 to adsorb appreciable quantities of *n*-paraffins compared with sodium zeolite A. This property of the new zeolite probably is related to the smaller number of sodium ions per unit cell compared with sodium zeolite A. When 30 to 40% of the sodium ions in zeolite A are replaced by calcium ions, the resulting zeolite is capable of adsorbing straight chain hydrocarbons. At this level of exchange the unit cell of zeolite A contains an average of 9.6 to 10.2 cations. These data suggest that perhaps the nine sodium ions in zeolite ZK-4 occupy sites in the lattice similar to those occupied by the cations in calcium exchanged sodium zeolite A. Studies are currently underway in an attempt to establish the location of monovalent cations in the new zeolite. As shown in Table II, the new sodium zeolite can separate straight-chain from branched-chain hydrocarbons and potassium zeolite ZK-4 can separate water from both straight-chain and branched-chain hydrocarbons.

(1) (a) D. W. Breck, W. G. Eversole and R. M. Milton, *J. Am. Chem. Soc.*, **78**, 2338 (1956); (b) D. W. Breck, W. G. Eversole, R. M. Milton, T. B. Reed and T. L. Thomas, *ibid.*, **78**, 5963 (1956); (c) R. M. Milton, U. S. Patent 2,882,243 (1959).

(2) R. M. Barrer and W. M. Meier, *Trans. Faraday Soc.*, **54**, 1074 (1958).

(3) J. V. Smith, *Acta Cryst.*, **7**, 479 (1954).

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REACTIONS OF THE *t*-NITROBUTYL ANION RADICAL

Sir:

Although the e.s.r. spectra of anion radicals of aromatic nitro and dinitro compounds have been studied,[1,2,3,4] no similar information is available for aliphatic nitro compounds. In contrast to the stable anion radicals derived from either sub-

(1) R. L. Ward, *J. Chem. Phys.*, **30**, 852 (1959).

(2) D. H. Geske and A. H. Maki, *J. Am. Chem. Soc.*, **82**, 2671 (1960).

(3) R. L. Ward, *ibid.*, **83**, 1296 (1961).

(4) A. H. Maki and D. H. Geske, *J. Chem. Phys.*, **33**, 825 (1960).

stituted or unsubstituted nitrobenzenes[2,5] or the isomeric dinitrobenzenes,[3,4] the anion radical derived from *t*-nitrobutane is unstable.

We have found that *t*-nitroalkanes form transient anion radicals which undergo relatively complex reactions.[6] As a result of detailed e.s.r. studies on anion radicals of *t*-nitroalkanes formed either by alkali metal or electrochemical reduction, some gross aspects of these reactions have become clear.

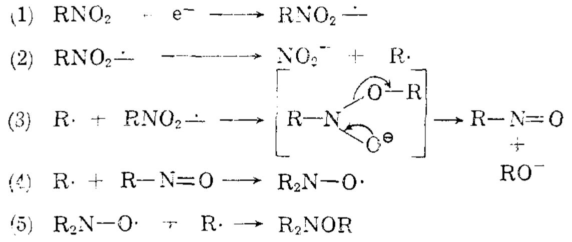
Polarographic reduction of *t*-nitrobutane in acetonitrile using tetra-*n*-propylammonium perchlorate as the supporting electrolyte proceeds cleanly by a one electron transfer. Identification of the product formed by one electron reduction of *t*-nitrobutane was accomplished by controlled potential electroreduction in acetonitrile within the microwave cavity of an e.s.r. spectrometer using the technique of Geske and Maki.[2] Electrolyses also were performed in the cavity using glyme and tetra-*n*-butylammonium perchlorate as supporting electrolyte. Electrolysis of *t*-nitrobutane in glyme led to an unstable paramagnetic species, most probably the anion radical of *t*-nitrobutane.

The spectrum in glyme consists of three equally spaced narrow lines of equal intensity. This spectrum is attributed to the isotropic hyperfine coupling of the unpaired electron with an N^{14} nucleus. The hyperfine coupling constant has the value 26.30 gauss. Any hyperfine interaction with the protons in the radical must have a hyperfine coupling constant less than the observed line width of 900 milligauss. On discontinuing the electrolysis, this spectrum fades to be completely replaced within seconds by a new spectrum consisting of a triplet of equal intensity distribution, but a hyperfine coupling constant of 15.45 gauss which is not subject to further change and which is identical with the spectrum of di-*t*-butylnitroxide[6] dissolved in glyme. Upon prolonged electrolysis the observed spectrum becomes a combination of the two, the triplet with hyperfine coupling constant of 15.45 gauss growing at the expense of the triplet with hyperfine coupling constant of 26.30 gauss. During the reaction of *t*-nitrobutane with sodium, however, only the triplet with hyperfine coupling constant of 15.45 gauss could be observed.

In contrast to glyme, electroreduction of *t*-nitrobutane in acetonitrile immediately produced two triplets with hyperfine coupling constants of 26.45 and 15.75 gauss. On discontinuing electrolysis, the 26.45 gauss triplet disappeared within seconds leaving only the 15.75 gauss triplet. A hyperfine coupling constant of 15.75 gauss corresponds to the hyperfine coupling constant for di-*t*-butylnitroxide in acetonitrile. This small change of coupling constant from that observed in glyme arises from the differences in solvent. Small changes of coupling constant with solvent have been observed previously.[1,2]

These observations strongly suggest that the anion radical of *t*-nitrobutane decomposes to di-*t*-butylnitroxide. The reaction of *t*-nitrobutane with sodium, therefore, like the reductive cleavage of triphenylphosphine oxide by sodium to diphenyl phosphinite anion and phenyl free radical,[7] is consistent with a similar interpretation, *i.e.*, as involving the collapse of a *t*-nitrobutyl anion radical to nitrite anion and a *t*-butyl free radical. Oxygen abstraction from *t*-nitrobutyl anion radical by *t*-butyl free radical can lead to the formation of *t*-nitrosobutane which by further reaction with *t*-butyl free radicals is converted to the nitroxide and trisubstituted hydroxylamine[8]

R = *t*-butyl.



$$(1)\quad RNO_2 + e^- \longrightarrow RNO_2\dot{-}$$

$$(2)\quad RNO_2\dot{-} \longrightarrow NO_2^- + R\cdot$$

$$(3)\quad R\cdot + RNO_2\dot{-} \longrightarrow \left[R{-}N{<}^{O-R}_{O^\ominus}\right] \longrightarrow R{-}N{=}O + RO^-$$

$$(4)\quad R\cdot + R{-}N{=}O \longrightarrow R_2N{-}O\cdot$$

$$(5)\quad R_2N{-}O\cdot + R\cdot \longrightarrow R_2NOR$$

This interpretation is supported by the observation that the reaction products comprise, in addition to nitroxide and trisubstituted hydroxylamine, sodium *t*-butoxide, sodium nitrite and small amounts of *t*-nitrosobutane. The demonstrated ability of the nitroso group to add free radicals to form trisubstituted hydroxylamines[10,11] supports equations 4 and 5 as reasonably depicting the source of both di-*t*-butylnitroxide and tri-*t*-butylhydroxylamine. Similar transformations to a stable nitroxide also have been observed for 2-nitro-2,4,4-trimethylpentane.

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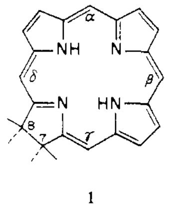
RECEIVED SEPTEMBER 15, 1961

A NEW ASPECT OF THE CHEMISTRY OF CHLORINS

Sir:

We wish to record the remarkable and hitherto entirely unrecognized fact that the chlorins (I) are extraordinarily susceptible to selective electrophilic attack at the γ and δ bridge positions. The phenomenon is most simply and forcefully demonstrated through proton magnetic resonance studies. The spectrum of chlorin e_6 trimethyl ester (II) contains three sharp low-field bands [at τ = 0.45, 0.64



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[5] A. H. Maki and D. H. Geske, *J. Am. Chem. Soc.*, **83**, 1853 (1961).

[6] A. K. Hoffmann and A. T. Henderson, *ibid.*, **83**, 4671 (1961).

[7] A. K. Hoffmann and A. G. Tesch, *ibid.*, **81**, 5519 (1959).

[8] Although *t*-nitrosobutane also might arise *via* attack of *t*-nitrobutane by *t*-butyl anion, Step 3 is preferred because no products corresponding to the attack of solvent by the strongly nucleophilic[9] *t*-butyl anion have been observed.

[9] P. D. Bartlett, S. Friedman and M. Stiles, *ibid.*, **75**, 1771 (1953).

[10] L. Phillips, *Proc. Chem. Soc.*, 204 (1961).

[11] B. A. Gingras and W. A. Waters, *J. Chem. Soc.*, 1920 (1954).