the β-configuration in the solid state were prepared by initiating with hexylammonium hydroxide to very low DP. We take as an example PBG prepared by initiating to DP 5.2. Solid films cast from different solvents show a single C=O amide frequency at 1628 ± 2 cm.$^{-1}$ characteristic of the β-form.[2] In solution, however, an additional C=O band is observed at 1658 cm.$^{-1}$ (chloroform), 1670 cm.$^{-1}$ (dioxane). This band appears to be associated with a solvated form since its frequency is solvent dependent. Both the 1628 and the higher frequency band appear at high concentrations (~20%) but upon dilution the 1628 band becomes progressively weaker until at 0.5% concentration only the higher frequency C=O band remains. The specific rotation in chloroform changes continuously with concentration from +18 at 5% to +2 at 0.75%, but in DCA shows a constant value of −14. The intrinsic viscosity is low: $[\eta]_{\mathrm{DCA}} = 0.056$.

The following conclusions may be drawn from these observations. (1) The α-helical configuration is the stable form of high molecular weight poly-γ-benzyl-L-glutamate dissolved in weakly interacting solvents such as chloroform. (2) In strongly interacting solvents such as dichloroacetic acid the configuration is that of a randomly coiled polymer: this is presumably due to strong solvation and is independent of molecular weight. (3) With very low molecular weight polymers in weakly interacting solvents, however, two forms exist. One of these is believed to be a solvated form because of the solvent dependence of the C=O amide frequency. The other form is the intermolecularly bonded β-form which upon dilution is converted to the solvated form.

We wish to thank Dr. B. Hargitay, Miss A. Asadourian, and Mr. R. H. Karlson for valuable discussions and experimentation related to this work.

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RECEIVED JULY 20, 1954

THE CATALYTIC DECOMPOSITION OF HYDROGEN PEROXIDE SOLUTIONS BY COMPLEX METAL AMMINES ADSORBED ON SILICA GEL

Sir:

The catalytic effect of cobalt and nickel sulfate adsorbed on the surface of silica gel upon the decomposition of a hydrogen peroxide solution has been reported to be only slight.[1]

Some of our recent work revealed that the complex metal amines of cobalt(II), copper(II), or nickel(II) adsorbed on the surface of iron-free silica gel very effectively catalyzed the decomposition of hydrogen peroxide solutions. When 1 g. of silica gel with its adsorbed metal ammine was placed in contact with 25 ml. of a 3% hydrogen peroxide solution, with or without its preservative, the decomposition was complete in 15 minutes at room temperature. A steady evolution of oxygen could be observed.

The complex metal ammines of silver(I), zinc(II), cadmium(II), or cobalt(III) adsorbed on the surface of silica gel failed to catalyze the decomposition of hydrogen peroxide solutions. Ammonia itself adsorbed on the surface of silica gel failed to effect any observable decomposition. It is of special interest to note that only those metal ammines characterized by unpaired electrons, hence paramagnetic, effected the decomposition of hydrogen peroxide solutions.

The adsorbed metal ammines that catalyzed the decomposition did not lose their activity with use. Samples of each were used on a fresh 3% hydrogen peroxide solution daily for a period of one month and were as active at the end of that period of time as they were at the beginning. The amount of the metal ammines adsorbed ranged from one to two millimoles per gram of silica gel. The metal ammines were prepared from metal nitrate solutions and concentrated ammonium hydroxide.[2]

Aqueous solutions of the nitrates of copper(II), cobalt(II) and nickel(II) produced little or no decomposition of 3% hydrogen peroxide, nor did aqueous ammonia solution itself. However, aqueous solutions of the complex ammines of copper(II), cobalt(II) and nickel(II) did produce rapid decomposition of the peroxide.

The same metal ions—cobalt, copper, nickel, silver, zinc and cadmium—coördinated with ethylenediamine or diethylenetriamine and adsorbed on the surface of silica gel, failed to give any noticeable catalytic decomposition of hydrogen peroxide solutions. Steric considerations and the stronger bonding of the metal ion to the ligand in these series may make it difficult for contact to be established between the hydrogen peroxide and the central metal ions of the adsorbed entity. The adsorption in these series ranged from 0.5 to 1.5 millimoles per gram of silica gel.

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[1] L. A. Nickolaw and Kobazeo, *J. Phys. Chem. U.S.S.R.*, **20**, 145–150 (1946).

[2] G. W. Smith, *J. Phys. Chem.*, **43**, 638 (1939).

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RECEIVED JULY 26, 1954

THE SYNTHESIS OF TERTIARY NITROPARAFFINS[1]

Sir:

While tertiary nitroparaffins have been known for a long time they have in no case been obtained by reactions which can be regarded as useful preparative methods.[2] We wish to describe the first practical synthesis of *t*-nitroparaffins, namely, the oxidation of *t*-carbinamines, RR′R″C–NH$_2$, to

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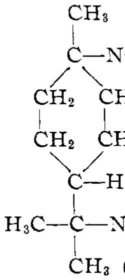
[1] This research was supported by the United States Air Force under Contract No. AF 18(600)-310 monitored by the Office of Scientific Research, Air Research and Development Command.

[2] In liquid phase nitrations, small amounts of hydrocarbon are heated with dilute nitric acid (generally around 130–150°) in sealed tubes which have to be opened for "periodic relief of pressure." Large numbers of sealed tubes are required, complex mixtures are produced, and the yields of *t*-nitrocompounds are poor [see, *e.g.*, S. S. Nametkin and K. S. Zabrodina, *Doklady Akad. Nauk S.S.S.R.*, **75**, 395 (1950); *C.A.*, **45**, 6998 (1951)]. Despite its great commercial importance, Hass' vapor phase nitration process can hardly be regarded as a laboratory synthesis, the more so since it gives rise to complex mixtures. And the reaction of silver nitrite with *t*-alkyl halides gives 0 to 5% yields of *t*-nitro compounds, B. Taub, Ph.D. Thesis, Purdue University, 1952.

RR′R″C–NO_2. This is readily accomplished by using potassium permanganate.

Thus far four amines have been oxidized; the permanganate oxidation of *t*-butylamine has been examined most thoroughly with the result that an 83% yield of pure *t*-nitrobutane has been obtained. Likewise, oxidation of *t*-amylamine gives analytically pure *t*-nitropentane (2-methyl-2-nitrobutane), *t*-octylamine (2-amino-2,4,4-trimethylpentane) yields pure *t*-nitroöctane and from 1,8-diamino-*p*-menthane the corresponding dinitro compound (I) is obtained.


(I)

In addition to its simplicity, this new method has the advantage of starting with *t*-carbinamines, substances which have recently become easily accessible.[3,4]

t-Butylamine (100 g.) was added to a stirred mixture of 650 g. of potassium permanganate and 3 l. of water in the course of fifteen minutes. The temperature rose to 45° and, after stirring for eight hours without external heating, the reaction mixture was held at 55 ± 5° for another eight hours. The product was isolated by steam distillation, washed with dilute hydrochloric acid, with water and then dried and distilled. A total of 117 g. (83% yield) of *t*-nitrobutane was collected as eleven fractions (b.p. 127–128°), all of which had $n^{28}\text{D}$ 1.3980 and m.p. 25–26°. *Anal.* Calcd. for $C_4H_9NO_2$: C, 46.59; H, 8.80; N, 13.78. Found: C, 46.46; H, 8.74; N, 13.55. Preliminary studies have shown that alkaline hydrogen peroxide is also a useful reagent for this oxidation.

This synthesis now makes *t*-nitroparaffins, *t*-nitrosoparaffins, and related compounds readily available so that for the first time a careful study of the chemistry of these substances is feasible. Such studies have been initiated in this Laboratory.

[3] J. J. Ritter and J. Kalish, THIS JOURNAL, **70**, 4048 (1948).

[4] We thank the Rohm and Haas Company for generous gifts of the amines employed here.

DEPARTMENT OF CHEMISTRY
PURDUE UNIVERSITY NATHAN KORNBLUM
LAFAYETTE, INDIANA RAYMOND J. CLUTTER

RECEIVED AUGUST 5, 1954

THE NATURE OF PARTICIPATION OF HYDROGEN IN SOLVOLYTIC REACTIONS

Sir:

The accelerating effect of β-hydrogen atoms on solvolytic reactions is well known. On the basis of rate retardation on substitution of deuterium for hydrogen, the acceleration has been ascribed to elimination-type driving forces in addition to the ordinary ionization process,[1,2] and to a carbonium ion stabilizing hyperconjugation, without reference to olefin formation.[3,4] By analogy to the participation of neighboring nucleophilic substituents, and to certain rearranging systems, the acceleration has been attributed to a similar participation of neighboring hydrogens, with the implication of a non-classical hydrogen bridged carbonium ion.[5]

Since the hydrogens on a methyl group para to a potential carbonium ion center are not eliminated in ordinary carbonium ion reactions and furthermore cannot be involved in bridged structures, we have studied this secondary isotope effect to choose among these alternatives.

Table I shows the results of measuring the rates of acetolysis of methyl-*p*-tolylcarbinyl chloride both with the normal isotope distribution and in the compound heavily deuterated in the α-methyl group (from which elimination may occur), and that deuterated in the *para* methyl group (from which elimination does not occur). The first-order rate constants are the slopes of a least-squares line derived from the titers at equally spaced time intervals according to Guggenheim as described before.[3,4] The maximum deviation of these rate constants from the mean of two or three runs is also shown. A roughly equivalent amount of sodium acetate was added to prevent reversal. It is clear that retardation results from deuterium substitution at both positions; that on the α-methyl group is more effective than that on the *para* methyl group. This constitutes the first example of change in rate produced by isotopic substitution at a point so remote from the seat of the reaction. We believe that this cannot be accounted for on the basis of elimination reactions at any stage, nor is the qualitatively similar nature of the effects at the two positions consistent with the assumption that the hydrogens on the α-methyl group are uniquely effective due to formation of a non-classical bridged ion. The possibility of isotopic exchange in the *para* methyl group of the intermediate carbonium ion is being considered.

TABLE I

RATES OF ACETOLYSIS OF METHYL-*p*-TOLYLCARBINYL CHLORIDE VARIOUSLY DEUTERATED

Compound	% D in CH_3 group	Temp., °C.	$k \times 10^4$ sec.$^{-1}$	$\Delta\Delta F^\ddagger$ per D cal./mole
$CH_3C_6H_4CHClCH_3$	0	50.25	1.14 ± 0.02	
$CH_3C_6H_4CHClCH_3$	0	65.30	6.02 ± 0.01	
$CD_3C_6H_4CHClCH_3$	67	50.25	1.04 ± 0.02	29 ± 7
$CD_3C_6H_4CHClCH_3$	67	65.30	5.61 ± 0.04	23 ± 7
$CH_3C_6H_4CHClCD_3$	80	50.25	0.892 ± 0.01	66 ± 5
$CH_3C_6H_4CHClCD_3$	80	65.30	5.15 ± 0.07	45 ± 5

The last column of Table I, headed $\Delta\Delta F^\ddagger$ per D is calculated from the expression

$$\Delta\Delta F^\ddagger \text{ per D} = \frac{2.303\,RT \log k_H/k_D}{3 \times \%\ \text{deuteration}}$$

The errors are estimated assuming a uniform 2% uncertainty in k_H/k_D. While this term is constant within experimental error for deuterium in the

[1] V. J. Shiner, Jr., THIS JOURNAL, **75**, 2925 (1953).

[2] V. J. Shiner, Jr., *ibid.*, **76**, 1603 (1954).

[3] C. E. Boozer and E. S. Lewis, *ibid.*, **74**, 6306 (1952); **76**, 794 (1954).

[4] E. S. Lewis and C. E. Boozer, *ibid.*, **76**, 791 (1954).

[5] S. Winstein, B. K. Morse, E. Grunwald, H. W. Jones, J. Corse, D. Trifan and H. Marshall, *ibid.*, **74**, 1127 (1952).