TABLE I

VALUES OF $\bar{D}_0$ AND A IN EQUATION (1)

Hydrocarbon	V_m, ml./mole	Temp., °C.	$D_0 \times 10^9$ (cm.^{2} sec.$^{-1}$)	A
n-Butane	101.4	25	1.17	28.0
		35	3.29	25.8
		46.5	7.54	22.8
Isobutane	105.5	25	0.53	28.8
		35	1.46	23.6
		46.5	3.75	19.0
n-Pentane	116.1	25	1.08	25.8
		35	2.59	24.7
		46.5	6.55	22.0
Isopentane	117.4	25	0.47	26.6
		35	1.34	22.5
		46.5	3.60	18.8
Neopentane	122.1	25	0.20	17.2
		35	0.60	14.5
		46.5	1.26	16.7

decrease from the smaller to the larger hydrocarbons. However, it is also evident that $\bar{D}_0$ is actually more influenced by the amount of branching than by the molar volume. Somewhat similar results have recently been reported by Park[4] for diffusion of various small molecules into polystyrene.

The temperature coefficient data fit the Arrhenius equation, $\bar{D} = B \exp(\Delta E^*/RT)$, since plots of log $\bar{D}$, for diffusion coefficients at a given concentration, *versus* $1/T$ give straight lines. Values of the Arrhenius parameters for $\bar{D}_0$ are given in Table II. As might be expected in view of the comparatively small variation in $\bar{D}_0$ with hydrocarbon, the values of the energy of activation do not vary widely, in fact by not much more than the estimated experimental error of ± 0.5 kcal. (± 1 kcal. for neopentane). However, there does appear to be a consistent trend in that ΔE^* values are lowest for the straight chain hydrocarbons and larger for the branched ones. These results show clearly that the diffusion is an activated process and are consistent with the notion that the slow step is formation of a hole in the polymer network.[2] However it should be noted that the variation of ΔE^* is surprisingly small in view of the considerable differences in the molar volumes and particularly in the minimal cross sectional areas of the molecules.

TABLE II

ARRHENIUS PARAMETERS FOR D_0 VALUES (CM.^{2} SEC.$^{-1}$)

Hydrocarbon	$10^9 D_0$, 35°	log B	ΔE^*, kcal.
n-Butane	3.3	3.4	16.7
Isobutane	1.5	3.6	17.5
n-Pentane	2.6	2.8	16.0
Isopentane	1.3	4.0	18.1
Neopentane	0.6	3.5	18

Values of energies of activation to compare with the above are available for polystyrene and polyvinyl acetate. For polystyrene, data are given by Park[5] for diffusion of methyl iodide ($V_m = 62$), methylene chloride ($V_m = 63$) and chloroform ($V_m = 80$). The calculated energies of activation vary with small molecule type and concentration and range from 14 to 27 kcal./mole. For polyvinyl acetate, values are available for acetone[6] ($V_m = 73$), propyl alcohol[7] ($V_m = 75$) and benzene[7] ($V_m = 89$ ml./mole).[7] For these three species, the energies of activation at zero concentration are 39, 41 and 37 kcal. per mole, respectively. Thus for diffusion into the two non-polar polymers the energies of activation are much lower than for the polar polyvinylacetate. This is the expected result since it implies that hole formation is considerably more difficult in a polar polymer.

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Irradiation of Liquid Ammonia[1]

BY RALPH ROBERTS[2] AND AUGUSTINE O. ALLEN

RECEIVED OCTOBER 10, 1952

Considerable evidence has been presented which has led to the concept of the existence of free electrons in alkali metal ammonia solutions.[3] Mass spectral data[4] indicate that ionization of ammonia to $NH_3^+ + e^-$ occurs more readily than any of the other possible ionization processes. Ionization along the path of the high energy bombarding ray has been postulated as one of the initial processes in the radiation effects of gamma and cathode rays. The above evidence led to an attempt to ascertain whether or not stabilized free electrons are formed by the high energy irradiation of liquid ammonia.

The ammonia was purified by distillation from a potassium solution in a suitable vacuum line. The sample for irradiation was collected in a conductivity cell with bright platinum electrodes. This was maintained at -70 to $-73°$ by using chilled acetone inside the cell holder and Dry Ice external to this. The holder was designed so that the thin wall of the cell could be directly irradiated with the cathode ray beam. The source of radiation was a 2-Mev. electrostatic generator constructed by the High Voltage Engineering Corporation, which can be operated to produce either 2-Mev. cathode rays or X-rays. The cell dimensions were such that the cathode ray beam did not penetrate to ammonia as far as the vicinity of the electrodes. In X-ray irradiations the entire cell was exposed. The cell constant was determined by comparison of the resistance of conductivity water in the cell with that observed in a cell with a known cell constant. A 1000 cycle a.c. bridge with earphones or cathode ray oscillograph was used to measure the resistance of the liquid ammonia. The experimental results are shown in Table I.

The data in Table I show no evidence for the formation of conducting species during the irradiation. Even though the ammonia used had a lower specific resistance than the literature value[3a] the impurity, in equivalents of alkali metal ion, was between 10^{-7} and 10^{-8} mole per liter. A change in conductivity equivalent to a concentra-

(1) Research carried out under the auspices of the Atomic Energy Commission.

(2) Office of Naval Research, Washington 25, D. C.

(3) (a) C. A. Kraus, THIS JOURNAL, **36**, 864 (1914); (b) S. Freed and N. Sugarman, *J. Chem. Phys.*, **14**, 295 (1946); (c) C. A. Hutchison and R. C. Pastor, *Phys. Rev.*, **81**, 282 (1951).

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TABLE I

CONDUCTIVITY OF IRRADIATED LIQUID AMMONIA

Volume NH_3, 8.3 ml.

Exposure, sec.	Dark time, sec.	Target current, μa.	Roentgens[a] × 10^{-7}	Sp. resist × 10^6	r./μa.-sec. × 10^{-6}
Sample 3, temperature −74°; 2 Mev. cathode rays					
0	..	..		1.50	
65	..	3.4	1.8	1.50[b]	0.68
...	30	..	...	1.50	..
...	65	..	...	1.50	..
30	..	10.0	2.4	...	.80
150	..	3.5	4.3	1.45[b]	.82
120	..	3.6	3.5	...	.81

Total exposure time, min.	Current, μa.	Roentgens total	Sp. resist × 10^3
Sample 4, temperature −75° to −72°; 2 Mev. X-rays			
0	...	0	510
2	100	6 × 10^3	490[b]
5	100	1.5 × 10^4	450[b]
Off 5	...	.....	450
6	100	1.8 × 10^4	460[b]
8	100	2.5 × 10^4	...
8'20"	...	.....	460
Off 4	...	.....	460

[a] Dose calculated assuming only one-half ammonia irradiated. [b] Measurement made during irradiation.

tion of about 3 × 10^{-9} mole per liter of alkali metal or free electron in liquid ammonia could have been detected. On the basis of the data, no evidence was obtained for the formation of stabilized free electrons during the irradiation of liquid ammonia under the experimental conditions used.

Acknowledgment.—One of the authors (R. Roberts) wishes to acknowledge the assistance of the Office of Naval Research and Brookhaven National Laboratory which made the conducting of this research possible.

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The Effect of Esterification on Anticholinesterases as Determined by Three Different Enzymes

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RECEIVED NOVEMBER 8, 1952

The preparation of 50 phosphonic and phosphinic acids has been described recently from our laboratory.[1] These compounds were examined for their anti-plasma cholinesterase activity.[2] Several of the compounds were found to be quite active. A few of the acids were esterified. Most of the esters were much more active against human plasma cholinesterase than the free acids. It is desirable for the development of insecticides to examine the action of anticholinesterases on enzymes of different species. In the present experiments we subjected our most active compounds to a comparative study using three different enzymes, human plasma cholinesterase, pig brain acetylcholinesterase and fly brain acetylcholinesterase. The effect of the esters on the cholinesterase activity of the three different soluble enzyme preparations has also been tested.

Methods and Materials.—The human plasma cholinesterase was the same as in our previous work.[2] The method for the preparation of soluble pig brain acetylcholinesterase has been described recently.[3] A similar procedure was employed for the preparation of acetylcholinesterase from the heads of the house fly (*Musca domestica* L.). An activator buffer–salt solution[3] was used in conjunction with the pig brain and fly brain acetylcholinesterase but not with the human plasma cholinesterase. Details concerning the enzyme inhibitor experiments have been described previously.[2,3] Residual acetylcholine was analyzed by Hestrin's[4] method using Klett–Summerson photoelectric colorimeter.

Inhibition of Three Different Cholinesterases.—It may be seen in Table I that our most active compounds are all

TABLE I

THE EFFECT OF ESTERIFICATION ON ANTICHOLINESTERASES AS MEASURED BY THREE DIFFERENT ENZYMES

Compound	I_{50},[a] moles/l. Plasma ChE	Brain AChE	Fly AChE
(*o*-BrC_6H_4)$C_6H_5PO_2H$	6 × 10^{-6}	7 × 10^{-3}	>5 × 10^{-3}
(*o*-BrC_6H_4)$C_6H_5PO_2CH(CH_3)_2$	1 × 10^{-6}	2.5 × 10^{-4}	2.5 × 10^{-6}
(*o*-BrC_6H_4)$C_6H_5PO_2C_2H_5$	1 × 10^{-5}	2 × 10^{-4}	5 × 10^{-5}
(*o*-BrC_6H_4)$C_6H_5PO_2CH_3$	8 × 10^{-6}	3.1 × 10^{-3}	>1 × 10^{-3}
(*o*-BrC_6H_4)$_2PO_2H$	1 × 10^{-4}	5 × 10^{-3}	>5 × 10^{-3}
(*o*-BrC_6H_4)$_2PO_2C_2H_5$	3 × 10^{-5}	2.5 × 10^{-5}	2 × 10^{-5}
o-$BrC_6H_4PO_3H_2$	4 × 10^{-3}	>5 × 10^{-3}	>5 × 10^{-3}
o-$BrC_6H_4PO(OC_2H_5)_2$	1 × 10^{-6}	1.25 × 10^{-3}	1 × 10^{-3}

[a] The I_{50} values (concentrations required for 50% inhibition) in this table were obtained from graphs in which % inhibition was plotted against the logarithm of the molar concentration of the compounds.

ortho-halogen derivatives. The *m*-halogen derivatives were less active, while the *p*-substituted compounds had no activity. The meta and para compounds are not included in Table I. It may be seen that esterification considerably increased the inhibitory power of the free acids in most instances. The isopropyl ester of (*o*-bromophenyl)-phenylphosphinic acid was more inhibitory than its ethyl ester and methyl ester. Concerning the plasma enzyme the ethyl ester of bis-(*o*-bromophenyl)-phosphinic acid was about 33 times more inhibitory than the free acid and the ethyl ester of *o*-bromobenzenephosphonic acid was 400 times more active than the free acid. When the pig brain enzyme was employed the ethyl ester of bis-(*o*-bromophenyl)-phosphinic acid was 200 times more inhibitory than the free acid and when the fly brain enzyme was tested the ester was at least 250 times more active than the free acid.

Among the 3 enzymes human plasma cholinesterase is much more readily inhibited by all compounds with the exception of ethyl ester of (*o*-bromophenyl)-phenylphosphinic acid, than the pig brain and fly brain acetylcholinesterase. This is not surprising since the plasma cholinesterase and the two brain enzymes belong to 2 different groups of enzymes.

Acknowledgments.—The authors are grateful to Drs. G. O. Doak and L. D. Freedman for the phosphorus compounds.

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Preparation of a Cyclopentenone by the Stobbe Condensation

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RECEIVED OCTOBER 8, 1952

The Stobbe condensation with two δ-keto-esters has been shown to give substituted cyclohexen-