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ELECTRICAL CONDUCTIVITIES OF ISOMERIC BUTYL BROMIDES

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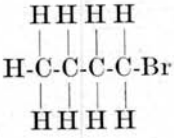
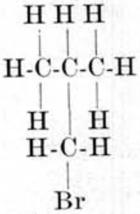
INTRODUCTION

Methyl groups are considered more electron-releasing than single hydrogen atoms. This means that the electron pair joining a methyl group to a given carbon is closer to that given carbon than is the electron pair joining a single hydrogen to the same given carbon. Such electron displacement can, to a degree, accumulate from several methyl groups and be transmitted along a carbon chain. If thus transmitted to a halogen atom, the electron displacement results in an increased tendency for the halogen to sever its connection and depart from the parent compound as an anion. (Desha, 1952: 43, 124).

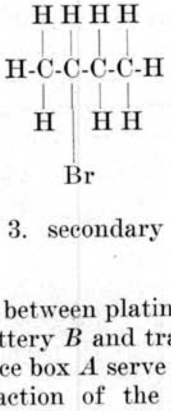
Four different isomeric butyl bromides exist — and their electrical conductivities should, from the foregoing considerations, increase in the order $1 < 2 < 3 < 4$. The experiments here reported were done to test this prediction.



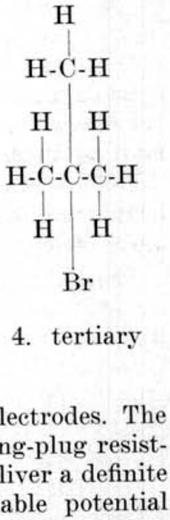
1. normal



2. iso



3. secondary



4. tertiary

APPARATUS

The apparatus of Sellers and Sulzbach (1955) slightly modified was used for measuring the conductivities of the butyl bromides. The fundamental parts of the modified setup are diagrammed in Figure 1. The organic liquid being tested is contained in an H-shaped glass cell *F*, between platinum electrodes. The battery *B* and travelling-plug resistance box *A* serve to deliver a definite fraction of the available potential difference, through *F* or bypassing it, according to the setting of switch *E*. The switch *D* allows the net resulting potential to be applied to the precision condenser *C*; *D* also may be set to let *C* discharge through the ballistic galvanometer *G* on depressing key *H*. *H* when released shunts *G* by a critical damping resistance

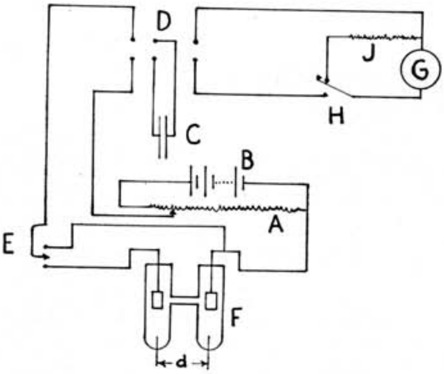


FIG. 1.—Wiring diagram of conductivity-measuring apparatus: A, potential divider; B, ten dry-cell batteries; C, condenser of known capacitance; D, short-throw double pole, double-throw switch; E, switch to by-pass H-cell; F, H-cell with platinum electrodes; G, ballistic galvanometer; and H, high-insulation contact key.

J, so as to stop G and make it ready for a new measurement in the minimum of time.

An air thermostat (with electric heating and circulation of air) and an electrical timer were employed.

The voltage of B must be great enough to send a small but definite current through F, sufficient to give a readable deflection of G in a reasonable time. The relation of R to B should be such that the square of the voltage divided by the ohmage never exceeds one-fourth watt.

The condenser used here was of 0.500 microfarads capacity, and the galvanometer had a sensitivity of about 10^{-9} coulombs per cm. deflection, A was 10,000 ohms, and B was sometimes as high as 15 volts. The thermostat temperature was 25.0 ± 0.5°C; the cell constant was 58.5. Wide variations in apparatus are permissible.

CHEMICALS

The four butyl bromides were prepared from corresponding alcohols according to methods of Adams and Johnson (1948: 199-201) and Gilman and Blatt (1951: 38-41) and purified until boiling points agreed well with those in the literature.

PROCEDURE

The sample was put in F in amount sufficient to fill the horizontal tube. The electrodes were installed centrally in their wells, with faces perpendicular to the axis of the horizontal tube, and centered upon it. The cell was put into the thermostat and allowed to reach temperature equilibrium. A voltage was provided at A sufficient to give through F a useful charge on C in 15.00 seconds, and allowed to act through F for this time interval. C was then discharged as punctually as possible through G, by manipulating D and H. The resulting deflection Θ was read. Then the process was repeated with F bypassed, and the voltage at A lowered, if necessary, by an aliquot fraction. The new deflection divided by the aliquot fraction (which might be unity) was recorded as Θ_0. The distance d between the electrodes in F was measured by simple sighting to a centimeter ruler. F's cross-sectional path area A was determined from micrometer measurements upon a glass rod which slip-fitted inside a piece of tubing like the horizontal portion. From the capacity c of the condenser in farads, the time of charge t in seconds, the deflections Θ and Θ_0 in centimeters, and d/A in reciprocal centimeters, the specific conductivity L of the sample was calculated. Formula a was used when Θ and Θ_0 were of the same magnitude and formula b otherwise.

$$(a)\quad L = 2.30\,\frac{cd}{At}\,\log_{10}\frac{\Theta_0}{\Theta_0 - \Theta}$$

$$(b)\quad L = \frac{cd}{At}\,\frac{\Theta}{\Theta_0}$$

DERIVATION OF WORKING EQUATIONS

Smith (1948:59-60, 107-108) gave essential details. In summary, the fundamental circuit contains a voltage source, a resistance and a condenser in series. At any instant, the sum of the three voltages across these circuit elements adds up to zero, according to Kirchoff's second law of circuits. The resistance's voltage, by Ohm's law, is its resistance multiplied by the current through it; the condenser's voltage is the charge on it divided by its capacitance. The current may be replaced by rate of change of charge with time, and the resulting differential equation rearranged and integrated. The integration constant is evaluated from initial conditions; charge is zero when time is zero. The resistance is the reciprocal of the conductivity. The specific conductivity is the proportionality factor between measured conductivity and the ratio of path area to path length; the ratio d/A is the cell constant. Combining all these ideas leads to equation a. Equation b has been derived by us, by taking the natural-logarithm prototype of a and dividing out the fraction beyond the log symbol. The fraction is expressed as $1 + \frac{\Theta}{\Theta_0 - \Theta}$ thereby. Then the second term of the denominator is dropped, the natural-logarithmic sum expanded in a Maclaurin series, and all terms but the first dropped.

RESULTS

These are shown in Table 1. Each number represents a mean of several closely-agreeing results, with checks by intervening repurifications.

TABLE 1.—Conductivity of Butyl Bromides.

	Θ_0	Θ	L
Normal butyl bromide	195.00	0.50	0.0050
Isobutyl bromide.....	194.00	0.80	0.0078
Secondary butyl bromide..............	195.00	44.50	0.502
Tertiary butyl bromide	194.50	2.95	0.0295

The secondary compound revealed no acid present when tested with moist litmus.

INTERPRETATION

The order of specific conductivity therefore is $1 < 2 < 4 < 3$ instead of the predicted $1 < 2 < 3 < 4$. We tentatively assume that the remarkably high specific conductivity of the secondary compound is caused by the "electron suction" of one of the partly electron-emptied methyl groups which can approach the bromide. Only in the secondary compound can one methyl group approach the bromine at a place remote from its valence while more than one feed electrons at short range along the chain.

ACKNOWLEDGMENT

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