Interaction of Free Radicals and Triethylborine

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LITTLE is known about such reactions as

$$R_nX + R' \rightarrow R + R_{n-1}R'X,$$

where R is an alkyl radical and R′ is either an alkyl radical or a halogen atom. The only such reaction so far investigated[1] is that between methyl radicals and dimethylmercury. We have investigated the interaction of free radicals with alkylboron compounds by gas-phase photolysis of azomethane, and biacetyl in the presence of triethylborine. Triethylborine did not give volatile material when photolysed alone or when heated in the dark below 90° with the other reactants. The volatile products were:

(*a*) With acetone; ethane, ethylene, propane, and butane.

(*b*) With azomethane; ethane, propane, and small amounts of butane.

(*c*) With biacetyl; (i) at low temperature, ethane, butane, and small amounts of uncondensables; (ii) at 50°, the same products and small amounts of propane.

These products are compatible with the following reactions:

$\mathrm{Me} + \mathrm{Et_3B} \rightarrow \mathrm{Et} + \mathrm{MeEt_2B}$ (1
$\mathrm{MeCO} \rightarrow \mathrm{Me} + \mathrm{CO}$ (2)
$\mathrm{MeCO} + \mathrm{Et_3B} \rightarrow \mathrm{Et} + \mathrm{MeCO{\cdot}Et_2B}$ (3)
$\mathrm{Me} + \mathrm{Et_3B} \rightarrow \mathrm{MeH} + \mathrm{C_2H_4Et_2B}$ (4)
$\mathrm{Et} + \mathrm{Et_3B} \rightarrow \mathrm{EtH} + \mathrm{C_2H_4Et_2B}$ (5)

We could not find any reference of compounds containing acetyl-boron bonds in the literature, but they could be postulated, at least as intermediates, because the B–C bond would be stabilized by the double bond located in the α position to the boron atom.

The average value for the disproportionation ratio found from runs with biacetyl at room temperature was 0·12 (from the runs with acetone a slightly higher value was obtained). This agreement with the accepted value not only shows that the postulated mechanism is in the main correct, but that the system is a potentially useful secondary source of radicals.

[1] R. E. Rebbert and P. Ausloos, *J. Amer. Chem. Soc.*, **1963**, **85**, 3086.

If we take the value for k_2 given by E. O'Neal and S. W. Benson,[2] k_3 is $= 1{\cdot}4 \times 10^9$ c.c. sec.$^{-1}$ mole^{-1}, which would give a very low energy of activation (lower than 3 kcal, if 10^{11} c.c. sec.$^{-1}$ mole^{-1} is taken for the *A* factor). The attack with a methyl radical (reaction **1**) seems to be 100 times slower at room temperature.

Reaction **5**' is faster than similar hydrogen abstraction from alkyl groups in other compounds.[3] At room temperature $k_4 = 5 \times 10^6$ c.c. sec.$^{-1}$ mole^{-1}. This points to a particularly active hydrogen atom (probably that α to the boron atom).

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[2] E. O'Neal and S. W. Benson, *J. Chem. Phys.*, 1962, **36**, 2196.
[3] A. F. Trotman-Dickenson, "Progress in Reaction Kinetics," Pergamon Press, Vol. 1, 1960, p. 107.