system should be small. Conversely, for determining trace amounts of substances with high partition coefficients the values of t should be large, and the size of the gas sample taken from the dilution system should be increased.

The system described here has been developed as a result of a recent improvement in the original vapour dilution technique described by Dr. J. E. Lovelock[1]. Such improvements are described in a paper to be published shortly by I. Fowlis and R. P. W. Scott.
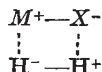
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Effect of Fluoride Ion on the Activation of Molecular Hydrogen by Silver(I)

ACCORDING to Halpern[1] the effect of complex forming ligands on the activation of molecular hydrogen by metal ions can be explained by the following scheme:

$$M^+ — X^-$$
$$H^- — H^+$$

Thus the heterolytic splitting of hydrogen is the consequence of the concerted action of the central metal ion and the ligand bond. Great activation effect can be expected from the ligands which, although weak acids, form unstable complexes with the metal ion, that is, which do not screen the positive charge partly responsible for the heterolytic splitting. These requirements are contradictory in general, being a parallelism between the proton affinity and the complex forming tendency of the ligands. In the case of silver(I), the reduction of which by hydrogen was thoroughly investigated by Halpern et al.[2-5], the fluoride ion fulfils the requirements mentioned: although hydrogen fluoride is a rather weak acid ($pK = 3.4$), the fluoride ion forms an unstable monofluorosilver(I) complex[6,7].

So the effect of fluoride ion on the reduction of silver(I) by molecular hydrogen seemed worthy of investigation.

The reaction was studied in an all-glass apparatus. Hydrogen was bubbled through the thermostatically controlled neutral solution (pH 6) of silver nitrate (up to 0.1 mole/l.) and potassium fluoride (up to 2.0 mole/l.). The reaction was followed by the titrimetric determination of non-reduced silver(I).

The fluoride ions increase dramatically the velocity of reduction. The results can be described by the following expression:

$$-\frac{d[H_2]}{dt} = \frac{1}{2}\frac{d[Ag^+]}{dt} = v = k.C_{Ag}\frac{K[F]}{1+K[F^-]}.[H_2]$$

where K is the stability constant of the silver fluoride complex[7]. Light has a small but definite enhancing effect. The velocity constants were calculated at different temperatures in the range of 30–70° C. The results are summarized in Table 1. For comparison some literature data referring to the aquo-complex and to the most effective amine complexes are also included.

Table 1

Ligand	log k (70°C)	$\Delta H \neq$	$\Delta S \neq$
H₂O	−3.2	23.3	− 6
CH₃-N(CH₂-CH₂)N(CH₃)₃	0.17	15.1	−14
N(CH₂CH₃)₃N	0.26	17.1	− 8
F (in dark)	0.79	18.3	− 3
F (in diffused daylight)	0.88	20.3	+ 4

Thus the fluoride ion is the most effective ligand so far found.

Considering that the configuration of silver(I) complexes is linear, and that the co-ordinated F⁻ and H₂ do not touch each other even being in adjacent position, the following scheme for the activated complex must be assumed:

F---Ag⁺ ---- H-
| |
H   H⁺
   \   /
      O
      |
      H
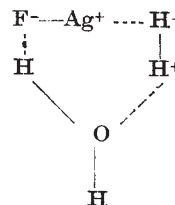
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Steric Effect in Mass Spectra of cis–trans Disubstituted Ethylenes

PREVIOUSLY[1-5] we reported results concerning the behaviour under electron impact of cis and trans isomers of disubstituted cycloalkanes. The steric effect in such compounds shows up by the fact that the ionized cis isomer is less stable than the corresponding trans one in derivatives of cyclopropane[1], cyclobutane[2], cyclopentane[3] and cyclohexane[4]. Those results are summarized in a recent paper[5].

In the same way we have investigated several pairs of cis and trans ethylenic isomers in order to check whether the same kind of relationship exists between mass spectra and stabilities of those isomers. Looking up the few data published in the literature[6] we found six pairs of cis–trans derivatives of butene with an increasing number of methyl groups on the two end carbon atoms.

We calculated the abundances I_{cis} and I_{trans} of molecular ions in percentage of total ionization. The results are listed in Table 1. These can be considered as a measure of the stability of the ionized compounds[7].

The figures in the last column of Table 1 indicate that within experimental uncertainties there is no difference between the stabilities of cis and trans 2-butenes. The same situation occurs in derivatives of butene substituted by one methyl group (2-pentene) or by two methyl groups,

Table 1. RELATIVE ABUNDANCES OF MOLECULAR IONS IN cis–trans DISUBSTITUTED ETHYLENES (PERCENTAGE TOTAL IONIZATION)

Pair No.	Name of the compound	Formula*	I_{trans}	I_{cis}	I_{trans}/I_{cis}
1	2-Butene	C—C=C—C	17.98	18.11	0.99
2	2-Pentene	C—C=C—C—C	9.71	9.62	1.01
3	4-Methyl-2-pentene	C—C=C—C—C (with C branch)	8.08	7.98	1.01
4	3-Hexene	C—C—C=C—C—C	6.97	6.85	1.02
5	4,4-Dimethyl-2-pentene	C—C=C—C—C (with 2 C branches)	6.52	5.96	1.09
6	5,5-Dimethyl-3-hexene	C—C—C=C—C—C (with 2 C branches)	4.19	3.42	1.22
7	2,2,5,5-Tetramethyl-3-hexene	C—C—C=C—C—C (with 4 C branches)	1.08	0.16	≈ 7

* H atoms omitted.