ion pair return

Also contains definitions of: external ion-pair return, hidden return, internal return

The recombination of a pair of ions $R^+$ and $Z^-$ formed from ionization of $RZ$. If the ions are paired as a tight ion pair and recombine without prior separation into a loose ion pair this is called 'internal ion-pair return':

$$
\begin{align*}
R^+ & \quad Z^- \\
\text{tight ion pair} & \quad \text{covalent molecule}
\end{align*}
$$

It is a special case of 'primary geminate recombination'. If the ions are paired as a loose ion pair and form the covalent chemical species via a tight ion pair, this is called 'external ion-pair return':

$$
\begin{align*}
R^+ & \quad || \quad Z^- \\
\text{loose ion pair} & \quad \text{tight ion pair} & \quad R^+ \quad Z^-
\end{align*}
$$

It is a special case of 'secondary geminate recombination'. When the covalent molecule $RZ$ is reformed without direct evidence of prior partial racemization or without other direct evidence of prior formation of a tight ion pair, (e.g. without partial racemization if the group $R$ is suitably chiral) the internal ion-pair return is sometimes called a 'hidden return'. External (unimolecular) ion-pair return is to be distinguished from 'external (bimolecular) ion return', the (reversible) process whereby dissociated ions are converted into loose ion pairs:

$$
\begin{align*}
R^+ & \quad + \quad Z^- \\
\text{RZ} & \quad \downarrow & \quad R^+ \quad || \quad Z^-
\end{align*}
$$

Source:
PAC, 1994, 66, 1077 (Glossary of terms used in physical organic chemistry (IUPAC Recommendations 1994)) on page 1127